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Book Reviews

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A REVIEW OF THE DURABILITY OF ROOFING BITUMENS *

By K. G. MARTIN †

SUMMARY

A review has been made of the literature on the durability of bitumens with regard to the performance of bituminous roofs. Oxidation is generally considered to be the most important factor, and particular attention has been given to the laboratory study of this reaction and the development of durability prediction tests.

It is proposed that three separate oxidation tests simulating conditions of application, exposure to moisture and air in the dark, and exposure to moisture and air in the light may be developed to assess roofing bitumens. Further chemical investigation of the functional groups of the less viscous fractions is required.

INTRODUCTION

BITUMENS deteriorate at a rate which is greatly dependent upon the function they perform and the conditions to which they are exposed. Extreme cases may be cited, for instance, very thin layers of Syrian natural asphalts exposed to light react fast enough to be used as the photo-sensitive ingredient of a photographic plate. At the other extreme, thick layers of Mesopotamian natural asphalts, which are quite similar, were used beneath massive stone and after 5000 years are still to be found intact.

A great amount of research into the phenomena of deterioration of bitumens has been carried out. A recent bibliography [1] lists about 400 references, mainly relating to bituminous roads. The purpose of this review is to make a critical examination of the main developments that are of interest in a study of the durability of bitumens in relation to the performance of bituminous roofs.

A complex range of bitumens exists [2] and four types are used in roofing, namely, naturally occurring asphalts, coal tar pitches, residual asphaltic bitumens, and blown asphaltic bitumens. These types have always been considered separately in the literature and are available in various grades of hardness. Considerable variation may occur within each type, depending upon the source of the original material and method of processing, but variation between types is usually more important, and reference to source has not always been made in published reports.

FACTORS CAUSING DETERIORATION OF BITUMINOUS ROOFS

Three main types of roof are recognized, multi-layer sandwiches of bitumen and bituminized fabric (built-up roofs), overlapping single-layer sheets of bituminized fabric (sheet roofs), and thick layers of voidless mixtures of bitumen plus mineral aggregates (mastic asphalt roofs). It has been common experience in several countries that the service life of these roofs is much shorter than the life of other components of the building, and a few surveys of the condition of roofs on existing buildings of known age and construction have been made to determine the factors responsible. In the U.S.A. most of the premature failures of all roofs were found by Waldron and Snoke [3] to be caused by faulty construction, including faulty flashings, rather than by severe weathering, and faulty materials accounted for only a minor proportion of failures. Sheet roofings with exposed surfaces of either bitumen or bitumen surfaced with mineral granules deteriorated more rapidly in warm humid climates, with much sunshine, and southern-facing surfaces deteriorated more rapidly than those facing north (northern hemisphere). Deterioration was also more rapid the lower the slope of the roof.[4]

In Sweden, early failures of built-up and sheet roofs were also caused mainly by faulty construction [5] resulting from insufficient knowledge of the best methods of application according to particular contingencies. The relatively rapid deterioration of the bituminized fabrics after the bitumen coatings had failed by weathering was also an important cause of failure.

In Australia, a survey made by the Division of Building Research is mentioned by Holmes [6] and, again, roof failures were attributed to faulty construction and poor design, as well as to weathering of exposed bituminous surfaces. It was suggested that shielding material, such as aluminium leafing paints, gravel, or concrete tiles, should be applied to all bituminous roofs. Similar experience and proposals had been reported from South Africa.[7]

Codes of practice designed to overcome the problem of faulty roof construction have been published in several countries [8–11] and methods of shielding to increase the service life of bituminous roofs were discussed in a recent study.[12] Shielding is obviously the first answer to the problem of durability, but the more efficient materials, such as *in situ* concrete, concrete tiles, and asbestos cement tiles, increase the cost of a roof, and the less expensive metal foils, mineral aggregates, and paints provide less efficient shielding. With improvement in construction and the avail-

* MS received 17 March 1961.

† Division of Building Research, Commonwealth Scientific and Industrial Research Organization, Highett, Victoria, Australia.

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ability of glass fibre roofing fabrics that are more dimensionally stable [13] and more resistant to deterioration by moisture,[14] the ultimate service life of bituminous roofs, particularly the lower cost constructions, becomes more dependent upon the durability of the bitumen.

WEATHERING STUDIES

Evaluation of the performance of bitumens in actual roofs is complicated by the long times necessary for significant results and the many variables, such as workmanship, weather during construction, degree of exposure, nature of roofing fabric, and roof design, that may influence performance. The Division of Building Research has constructed 22 experimental built-up roofs containing almost 200 experimental sections with 20 different bitumen binders, and as a minor interest the performance of the bitumens has been visually evaluated at regular intervals by a system of numerical ratings, but no statistically significant conclusions have been reached because of the large number of variables and the difficulty of assessing the condition of the bitumen.

Laboratory examination of small specimens of bitumens that have been directly exposed outdoors has been more fruitful. Toch [15] exposed films of hard bitumen beneath coloured glasses and found that rapid surface deterioration occurred beneath violet, only slight beneath green, and little beneath red. When air and moisture were excluded, no deterioration occurred beneath any of the glasses, and deterioration by oxidation of the surface accelerated by light was postulated. Similar exposures beneath clear glass [16] showed that softer bitumens hardened considerably and became more insoluble in organic solvents after exposure. The exposure tests were extended to a wide range of bitumen types, and the effect of volatilization was evaluated.[17,18] It was found that volatilization played only a minor role, but that increased intensities of heat and light were responsible for more rapid changes. The bitumens were shielded to prevent contamination with dust, but this meant precluding the effects of precipitation. Graefe [19] showed that leaching by rain water occurred when bitumen coatings were completely exposed, and an insoluble bleached surface layer was produced. Further observations of exposed coatings [20] indicated the importance of the physical properties of the bitumen, and the likelihood of cracking of the photo-oxidized surface as a result of rapid changes of temperature. Although not fully realized at the time, the two processes that cause the failure of exposed bituminous coatings were thus elucidated, namely, photo-oxidation causing formation of water-soluble products that lead to erosion, and photo-oxidation and volatilization causing hardening of the surface, leading to cracking under thermal or mechanical strains. A final important contribution from observations of exposure tests was made by Benson,[21] who showed that fairly rapid changes could be detected with a microscope if very thin translucent films (*ca* 25 μ) were exposed. He described the changes, the most important of which was coagulation, but no attempts were made to evaluate the changes chemically or mechanically.

Numerous workers consider that outdoor exposure tests are unsuitable because of the long times involved and the lack of reproducibility of the weather. Artificial weather machines that accelerate the deterioration under controlled conditions were used and much useful work has been accomplished with them. The characteristic weathering behaviour of various asphaltic bitumens was reproduced in the laboratory,[22] and the function of light, particularly the shorter wavelengths which most accelerate the oxidation by air, and water, which leaches certain oxidation products, was generally elucidated.[23] This work was repeated using certain coal tar pitches, and it was reported [24] that less water-soluble material was formed by the pitches than by an asphaltic bitumen. Correlation of an artificial weathering test with outdoor exposure was claimed to be good for certain sheet roofings,[25] and the test was included in ASTM Standards as a recommended practice (D529-39T). Another artificial weathering test was found to be useful in evaluating the behaviour of mastic asphalt roof membranes.[26] However, according to a survey by Neppe [27] the weatherometers were not widely accepted because controversial results were often found, particularly in attempts to correlate tests with actual serviceability under various climatic conditions. The basic difficulty is that the weather is too complex and too variable to be accurately assessed and reproduced in a way that accelerates all important factors to the same degree. Reinhart [28] considered that outdoor exposure tests are not reproducible unless carried out for several years and at several localities for one climate. He also pointed out that solar radiation characteristics vary with time of day, season, orientation of surface, altitude, latitude, and local atmospheric opacity, and cannot be accurately simulated by lamps whose characteristics vary off the production line and with age.

Weatherometers can give useful comparisons and have been used successfully at the National Bureau of Standards.[29] Recent developments have been reported by Kleinschmidt and Snoke,[30] who examined thin layers of two blown asphaltic bitumens exposed on aluminium plates in the weatherometer and outdoors. The surface film developed by oxidation accelerated by light was shown to be insoluble in common solvents but partly soluble in water; if left undisturbed it eventually cracked because it could not follow volume changes in the sub-stratum. Further oxidation of bitumen beneath the intact surface film was retarded,

but the surface cracks widened and grooving eventually extended through the layer. Water applied regularly eroded the surface film evenly, producing a matt appearance. The bitumen that formed the least amount of products soluble in water and lost least weight had the better performance record. The elution of water-soluble oxidation products was greater per unit area for thicker films, and certain components were decreased more than others in the whole bitumen. A process of migration of oily constituents to the surface to replace those constituents that had been photo-oxidized and leached was postulated. Similar migration in blown asphaltic bitumens is well known [31] and an oily phase can be extracted by placing loose limestone powder on the surface of the bitumen, the migration being analogous to syneresis of the intermicellar phase of colloidal gels.

EFFECTS OF HEATING

The liquefaction of bitumens by heating causes them to harden as a result of loss of volatiles and oxidation of the surfaces exposed to air. Laboratory performance tests involving the heating of bitumens under controlled conditions and measuring the hardening in various empirical ways have been devised. Lewis [32] showed that the heat tests could not be used to predict the amount of hardening of asphaltic bitumens caused by outdoor exposure, because biased importance was given to the volatilization process. Evaporation during outdoor exposure was found to be a very minor factor in the hardening of asphaltic bitumens, but of greater importance for coal tar pitches.[33] In general, it may be considered that heat tests on bulk samples predict only the order of changes to be expected when bitumens are heated during application, and particular conditions of test should be used to simulate particular applications. The important variables are layer thickness, exposed surface area, and temperature. A standard method of test for roofing bitumens is specified by the ASTM (D6-39T), but the temperature of the test is too low and is constant irrespective of the varying grades of bitumen. It has been pointed out [34] that the test temperature should vary according to the optimum temperature at which the bitumen is applied, and an empirical means of assessing this has been given.

One other effect associated with heating is the continued hardening of bitumens at room temperatures during storage. This was first demonstrated in 1897 by Dow,[35] but was not closely investigated until much later.[36,37] The effect was shown to be most prominent with fatty acid pitches, and air-blown asphaltic bitumens hardened more rapidly than residual asphaltic bitumens. It was considered to be due to the development of internal structure. Reheating and mechanical working partly or completely removed the hardening, depending upon the length of time the bitumen had been left undisturbed. If left for several thousand hours or more the hardening became partly permanent because some material had volatilized. The addition of fine mineral aggregate did not have any influence. Lee and Markwick [38] demonstrated similar hardening with mixtures of coal tars and aggregates, the tars from coke ovens showing the most prominent effects because they had constituents that slowly crystallized.[39] Little attention has been given to this phenomenon in connexion with hardening of bitumens on roofs.

PHYSICAL ASPECTS OF OXIDATION

Apart from field studies of actual roads, most reports on the durability of bitumen are concerned with oxidation, but only the more recently published need be mentioned. Numerous earlier workers reasonably considered that the susceptibility of bitumens to oxidation was directly related to durability, but all the proposed methods of oxidation had serious drawbacks. In some tests the bitumens were oxidized in solution and the physical constitution was ignored; in some the consequences of oxidation most important in practice (*e.g.* hardening) were not taken into account, and in others the conditions of oxidation were such as to induce a vastly different reaction from that which occurs in weathering. Most investigators attempted to devise short-term oxidation tests to give information on the ability of various bitumens to resist weathering, but they did not have much understanding of the oxidation process.

The first more fundamental studies were made by Dickinson and Nicholas [40] on the oxidation of coal tar oils in the dark. The rate of absorption of oxygen, the chemical products, and the effects of temperature and pressure were investigated. It was found that about half of the oxygen absorbed at 65° C was bound in the oils and the remainder was evolved as water and carbon dioxide. The overall rate of reaction was auto-retardant, and it was concluded that two simultaneous first order reactions were occurring—the conversion of phenols to resins, which was initially rapid but reached virtual completion, and a slower but continuous oxidation of hydrocarbons containing active hydrogen. Temperatures greater than about 65° C were found to alter the nature of the oxidation. The work was extended to coal tars,[39] and a laboratory pressure oxidation test was developed to evaluate different tars in terms of change of Fraass brittle point. The rate of absorption of oxygen at atmospheric pressure in the dark by thin films of coal tar was also studied and found to be markedly dependent upon film thickness. Below 0·2 mm the absorption of oxygen per gram of tar was constant, but at the greater thicknesses used in roofing work the rate decreased rapidly, and at 4 mm it was only one-tenth of that at 0·2 mm. This suggested a reaction con-

trolled by diffusion, and the theoretical interpretation was found to fit the experimental results. Asphaltic bitumens were included in further extension of the work,[41] and it was found that residual types absorbed oxygen at a slower rate than coal tars. As expected, the rate of absorption was slower with bitumens of higher viscosity and became faster at higher temperatures, the rate being approximately doubled for a temperature increase of 10° C. The Arrhenius relationship (exponential variation of absorption rate with absolute temperature) was obeyed, although the acceleration was due to several factors. Van Oort [42] also gave a detailed mathematical description of the auto-retardant rate of oxygen absorption in the dark by thin films of asphaltic bitumens. At temperatures up to 50° C the oxygen was quantitatively bound, whereas oxidation at 100° C caused the elimination of water.[31] The mechanical consequences of oxidation were investigated, but were only significant in reasonable times if films of the order of 10 μ were exposed. A simple shear plate microviscometer was constructed to evaluate the small quantities involved, and a means of calculating the elastic modulus from vibrational tests was also developed. Increased hardness due to oxidation was expressed in terms of increased stiffness, which is an elastic modulus dependent on time and temperature and was conceived by van der Poel.[43] Oxidation as an agent of weathering was considered to promote rupture of bitumen when the stiffness exceeded a critical value in relation to some operative strain, the magnitude of the increase of stiffness at the conditions of time and temperature of the strain being the important criterion. Long-term loadings such as thermal stresses are considered to be more important than impact or vibrational loads in connexion with the durability of roofing bitumens, and evaluation of changes of stiffness with the microviscometer would be pertinent. Van Oort [42] (Fig 45) showed that the amount of hardening was proportional to the amount of oxygen absorbed, and indicated that the best way to accelerate oxidation without changing the type of reaction was to increase the oxygen pressure. Van Oort's description of the absorption process has recently been re-examined [44] and, using a theoretical treatment similar to that of Lee and Dickinson,[39] the oxidation in the dark has been interpreted in terms of solubility, diffusion, and reaction constants of oxygen with bitumen, and the layer thickness. The reactivity of various asphaltic bitumens with oxygen was dependent upon source, type, and temperature; residual and blown bitumens had about the same reactivity, but a cracked bitumen was far more reactive. A rise of temperature of 10° C increased the reactivity by a factor of more than 2. The hardening was found to extend to more than 1 mm beneath the exposed surface, and the cracked bitumen hardened more than the residual or blown type. A naturally occurring asphalt also hardened more, but only after long periods of oxidation. Acceleration of the oxidative hardening by increasing the pressure of oxygen was examined and found to give a fairly constant acceleration factor for various grades and types of asphaltic bitumen. A simpler method [45] of accelerating oxidation by heating very thin films of bitumen in air at 107° C was shown to give a similar correlation with actual road performance as the pressure oxidation method, except for a bitumen with a high content of volatiles. This indicates that the main complicating factor to accelerating the oxidation in the laboratory by increasing the reaction temperature is evaporation, and not change in the type of reaction.

The increase in the rate of absorption of oxygen at room temperatures by films of asphaltic bitumens, due to exposure to light, was first investigated by Thurston and Knowles.[46] Only half of the absorbed oxygen became chemically bound, the remainder being eliminated as water and carbon dioxide. Similar behaviour was found with coal tars,[39] and the rapid formation of a surface skin that retarded evaporation was noted. It was later found [41] that the intensity of the light determined whether or not a surface skin would form, and that if the skin did form it retarded diffusion of oxygen into the bitumen. Irrespective of skin, the photo-oxidation extended to only about 10 μ beneath the surface. In the dark the coal tars absorbed oxygen at a greater rate than asphaltic bitumens, but light accelerated the absorption by the asphaltic bitumens most, the acceleration factor being between 100 and 200, presumably for an intensity of light similar to that of direct sunlight. Temperature increased the rate of absorption in a similar way as in the dark—a factor of about 2 for every 10° C. Similar acceleration of the absorption of oxygen into films of asphaltic bitumen at 50° C have been reported;[44] more than half the effect was shown to be due to light of wavelength between 2·8 and 3·6 μ. The amount of oxygen bound in the bitumen was only about one-third of that absorbed, so that more gaseous products were evolved than at room temperatures. A final difference to the reaction in the absence of light was that the hardness of the bitumen had little effect on the rate of reaction, so that diffusion of oxygen into the layer did not determine the rate of the process.

CHEMICAL ASPECTS OF OXIDATION

The chemical constitution of bitumens is extremely complex; they are mixtures of predominantly hydrocarbons of a wide range of molecular weight with varying paraffin, *cyclo*paraffin, and aromatic character. Oxygen, nitrogen, and sulphur are invariably present in smaller amounts, but bound as the more reactive functional groups. It is therefore not surprising that most reports on the weathering of bitumens from a chemical point of view are concerned with chemical additives. Abraham [2] lists the following additives

for improving durability; amines such as aniline, dimethyl aniline, and phenyl beta naphthylamine; phenols such as catechol, guaiacol (and hydroquinone); nitrogenous bases such as pyridine, quinoline, and nicotine; organic salts such as titanium phthalate and sodium lauryl sulphate; acids such as oleic, montanic, and various other fatty acids; sulphur compounds such as the phosphorus sulphides and aminomercapto-benzo-thiozole; finally, numerous inorganic powders that are commonly referred to as fillers or stabilizers. It is also of interest to note a patent in which the addition of rubber to bitumen is claimed to *increase* the sensitivity to light.[47]

Concerning more fundamental aspects, Walther [48] exposed films of asphaltic bitumens in sealed glass tubes outdoors and then measured the amount of solids insoluble in carbon tetrachloride; the amount of insolubles increased when water was present, but none were formed in the absence of oxygen. Peroxides were detected in the insoluble solids, and it was concluded that the organic peroxides were formed by oxidation and that these decomposed and polymerized. The conclusion was substantiated by showing that known inhibitors to the postulated type of reaction, such as hydroquinone and β-naphthol, retarded the formation of insolubles in carbon tetrachloride. It was known that photo-chemical reactions had a high probability of producing free radicals, and the acceleration of the oxidation by light was evidence of a free radical chain process. Dickinson and Nicholas [49] did not detect peroxides in oxidized tar oils but still considered the oxidation to be a free radical chain process via a hydroperoxide as primary product. This mechanism is generally accepted to describe the air oxidation of hydrocarbons [49] and may be described as follows:

Compounds containing active hydrogen atoms oxidize directly to the hydroperoxide. For instance, the mechanism for olefins is considered to be

$$RCH_2\,CH{=}CHR \xrightarrow{O_2} RCH(OOH)\,CH{=}CHR$$

and for saturated hydrocarbons a slower thermal reaction proceeds which is more rapid if the oxygen is excited by radiation

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot$$

The chain process is initiated by

$$ROOH \longrightarrow RO\cdot + OH\cdot$$
$$RO\cdot + RH \longrightarrow ROH + R\cdot$$
$$OH\cdot + RH \longrightarrow H_2O + R\cdot$$
$$HO_2\cdot + RH \longrightarrow H_2O_2 + R\cdot$$

and propagated by

$$R\cdot + O_2 \longrightarrow ROO\cdot$$
$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

and terminated by combination of free radicals or by inhibitors that capture peroxy radicals

$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$
$$ROO\cdot + A\cdot \longrightarrow x$$

Various workers have reported that the final products of oxidation are carboxylic acids, carboxyl and hydroxy compounds, and esters. The presence of carboxyl and hydroxyl groups in the final products indicates that the peroxy radicals decompose to oxy radicals whose usual chain-terminating step is via a slow transfer of hydrogen atoms,

$$i.e.\quad 2ROO\cdot \longrightarrow 2RO\cdot + O_2$$
$$2RCH_2O\cdot \longrightarrow RCHO + RCH_2OH$$

Most of the oxidation of coal tars was found to be associated [49] with active hydrogen atoms, and instability of the hydroperoxide above a certain temperature was considered to explain the change in nature of the dark oxidation with increase of temperature. The known ability of phenols to capture free radicals was also considered to lead to the preferential oxidation of phenols rather than the hydrocarbons. A highly significant correlation between phenol content and both resin formation and rate of oxygen absorption was found.

Phenols are known chain terminators, and a note of explanation on this aspect is warranted. Chain-terminating type inhibitors that most easily donate a hydrogen atom to free radicals are the most effective, but if the inhibitor hydrogen atom is too loosely bound it can also be removed by direct oxidation, particularly in autoxidizable substrates, to initiate further free radicals and further oxidation,

$$i.e.\qquad AH + O_2 \longrightarrow A\cdot + HO_2\cdot$$

Chain terminators are thus also chain propagators, and are seldom efficient anti-oxidants, because the rate at which they react with free radicals and the rate at which they autoxidize depend upon the same feature in their chemical constitution. Other types of anti-oxidant additives have been investigated, particularly peroxide decomposers.[49] One of these additives (phenothiazine) has been shown [51] to reduce the loss of water-soluble products to a marked degree and to improve the durability of an asphaltic bitumen when exposed in accelerated weatherometers.

The Road Research Board [52, 53] considered it advisable to remove the phenols from coal tars, and although this is done economically by pre-oxidizing with air containing ozone,[54] a new method, washing with alkali, was tried. An interesting anomaly arose because the tars washed with alkali gave improved Fraass brittle points after pressure oxidation tests, but thin films of these tars absorbed more oxygen than before. This can be explained by analogy with the findings of Ingold and Puddington,[55] who obtained an insoluble deposit when petroleum oils were oxidized,

and when the oxidation was repeated in the presence of alkali the deposit was suppressed but the oxygen absorption was increased. It was found that organic acids were produced by the oxidation and normally reacted with other constituents to form insoluble esters, but in the presence of alkali the acids were neutralized and esterification was prevented. It is known that the oxidative hardening of bitumens is associated with formation of insoluble products, and formation of ester has been detected in oxidized coal tars [40] and in asphaltic bitumens [56] oxidized by blowing with air at temperatures from 150° to 300° C. Goppel and Knotnerus [57] found that the ester linkages in air-blown bitumens largely contributed to formation of material of higher molecular weight, and became more numerous as the temperature of oxidation was reduced. Bitumens extracted from naturally-occurring rock asphalts also have very high ester contents.[58] It is therefore likely that ester formation, rather than polymerization, contributes to the development of insoluble products when bitumens are oxidized at temperatures occurring on roads and roofs. Most of the oxygen in water-soluble products of weathered asphaltic bitumens has been found to be present as polycarboxylic acids and polyhydroxy phenols [59] and, despite the leaching, the oxygen content of the bitumen was doubled, indicating that much of the oxidized material did not become water soluble. It is conceivable that the acidic products of oxidation are partly neutralized and bound in the bitumen as esters, and partly left as free acids that may be removed by washing with water. As the temperature of reaction increases and in the presence of light (when the oxidation is confined to the surface) the carboxylic acids tend to decarboxylate, evolving carbon dioxide, and water evolves as a result of condensation reactions.

The influence of sulphur upon the durability of bitumens is interesting. It was first reported [60] that the presence of sulphur increased the rate of oxidation of bitumens. However, the effect may have been due to the action of sulphur itself, which reacts with bitumen in a similar way to oxygen and causes it to harden, to become less susceptible to temperature, and to be less ductile.[61] More recently it has been claimed [62] that the addition of sulphur retards the oxidative hardening of bitumens, but the conditions of exposure used in this work were not similar to those met in practice. A correlation between sulphur content and constituents of asphaltic bitumens insoluble in pentane has been found [63] for asphaltic bitumens from six sources. The pentane insolubles are known to increase with age hardening, and it has been proposed that bitumens with higher sulphur contents will age harden less in practice because the chemical reactions have already taken place before the bitumen has been applied. However, the data provided in support of the proposal concern only two asphaltic bitumens, whereas other workers [64] have found no significant correlation between sulphur content and age hardening of asphaltic bitumens extracted from roads after service for nine years. It is known [44] that sulphur is associated with oxidative hardening, and most of the oxygen absorbed by films of asphaltic bitumen during the first stages of exposure in the dark is bound as sulphoxide groups which decompose in time to carbonyl compounds and mercaptans. Only a small part of the sulphur is involved, and the nature of the sulphur compounds in the bitumen is important. Sulphoxides of low molecular weight are believed to increase the dispersion of the micelle complexes and would also influence the hardness of bitumen. Certain organic sulphur compounds are well-known inhibitors of free radical chain processes and have been shown to improve durability and to retard the loss of weight of thin layers of asphaltic bitumens exposed in accelerated weathering machines.[51] The magnitude of the effect varies greatly, depending upon the source of bitumen and the chemical constitution of the additive. Presumably some sulphur compounds present in some bitumens are inhibitors of oxidation and others are initiators. The addition of further anti-oxidants has effects of varying magnitude, depending upon whether or not inhibitors are originally present. Sulphur compounds are also metal deactivators, and metallic oxides are known to catalyse oxidation of bitumen. Since bitumens invariably contain minute amounts of metals, usually iron and vanadium, sulphur compounds may also retard oxidation in this way.

The influence of both organic and inorganic additives upon the weathering of bitumens is usually small compared with the variability between bitumens of different type and source,[51, 65] and explanation of this variability is being sought in terms of chemical constitution. Asphaltic bitumens have been exposed to outdoor weathering and then fractionated, and the changes in the various fractions determined by infra-red absorption spectroscopy,[66] but this added little information to that obtained by ordinary chemical methods. By far the most important factor (although not stated by the author) was not chemical but physical, and this was that the fractions of lowest viscosity were attacked most. The fractionation of the bitumens was not a sharp chemical separation, but yielded components with progressively higher viscosities, and the fraction of lowest viscosity was most affected by the weathering, despite the fact that it contained the lowest amount of the reactive chemical entities. Heteroatoms oxygen, nitrogen, and sulphur were mainly found in the fractions of higher viscosity, which were little affected by the weathering, so that the degradation of the low molecular weight predominantly hydrocarbon fraction is the most important reaction. Of these hydrocarbons the aromatic groups, the highly branched chain structures, the oxygenated groups, and the *cyclo*paraffins were found to be most reactive. Infra-red spectra of a large

number of unfractionated asphaltic bitumens from different sources has shown [67] that the spectra are remarkably similar, in spite of which the bitumens varied widely in durability; the only correlation between durability and chemical constitution was that the less durable bitumens contained more hydroxyl groups than the more durable.

DISCUSSION

The outstanding problem concerning durability of bitumens is how to select the best type and grade for a particular roofing application. The answer lies in the use of laboratory prediction tests, and it is considered that suitable tests are now available. These tests may be considered as oxidations under conditions that simulate particular exposure hazards, and it is proposed that a combination of the following three separate tests is required to assess roofing bitumens:

(1) Heating bulk samples at temperatures of application.

(2) Oxidation of thin films in the dark and in the presence of moisture.

(3) Oxidation of thin films in the light, with washing of the surface by water.

A test of the first type has been developed by the ASTM, but a modified version [34] is preferable for assessing a wide range of bitumens.

The second type of test has been developed for coal tars [39] and for asphaltic bitumens,[42,44] the oxidation being accelerated partly by a small increase of temperature and mainly by using oxygen under pressure. The test has been developed for the softer bitumens used in road construction, and in applying it to the harder roofing bitumens the more complex rheological behaviour will need particular attention. The influence of moisture in the reaction vessel has not been reported and also needs to be investigated.

The third type of test has been developed by the National Bureau of Standards,[68] which uses the accelerated weatherometer that provides what is probably the most important durability test for roofing bitumens. However, these machines are costly, the reproduction of solar radiation is suspect, and the development of cycles that correlate with actual exposures for particular climatic regions would require many years of endeavour. It is proposed that a simpler test involving direct exposure of very thin bitumen films may be developed instead. Changes in weight, composition, and viscosity can be determined on very small amounts, and the time required to give significant changes would not be excessive if very thin films (*ca* 10 μ) are exposed. Solar radiation is by far the most important variable of the weather, and it is proposed that the exposure times be defined in terms of total intensity of radiation received. There is evidence [6] to indicate that the relative proportions of ultra-violet and heat components of solar radiation are fairly constant, and the fact that certain localities receive more ultra-violet radiation is simply because more total solar radiation is received and the intensity varies. The influence of both photo-chemical and heating effects should be sufficiently reproducible from test to test independent of actual solar time.

The most important factor that determines the service life of bitumen is the degree of exposure to solar radiation, and only completely exposed or completely shielded conditions have been investigated. Further exposure tests are warranted to provide information on the effects of the various shielding treatments used in practice and to provide a basis for evaluating the laboratory prediction tests. Despite the slow rates of change that may occur, changes in composition and consistency may be used to evaluate the exposed specimens and should be readily detected within reasonable times if very thin films are examined.

Chemical changes due to weathering of bitumens are not completely understood, but this is not surprising in view of the complex chemical nature of the materials. Modern spectrometric methods are being used in an effort to characterize the types of molecules that are present,[69–72] but only general trends for each particular type and source of bitumen have been revealed. Concerning the chemical constitution in relation to properties influencing durability, it is considered that the direct investigation of functional groups, as done by Goppel and Knotnerus,[57] would be more rewarding. It is apparent that the less viscous fractions are most concerned, and further chemical investigation might continue the work of Dickinson and Nicholas [40] by studying the constitution and oxidation of the oily fractions of various bitumens, particularly since a great amount of knowledge may be drawn from that accumulated on autoxidation of pure hydrocarbons, lubricating and paint drying oils.

References

1 Boas-Traube, S. Road Research Laboratory, Library Bibliography No. 84/SBT, 1957 (unpublished).

2 Abraham, H. "Asphalts and Allied Substances," 5th Ed. New York: D. Van Nostrand Co. Inc., 1945.

3 Waldron, L. J., and Snoke, H. R. National Bureau of Standards, Washington, 1940. Report BMS 57.

4 Snoke, H. R., and Waldron, L. J. National Bureau of Standards, Washington, 1942. Report BMS 84.

5 Hanson, R. *Byggmästaren*, 1953, **3**, 72.

6 Holmes, B. M. CSIRO Div. Build. Res. Rep., 1951.

7 Jennings, J. E., Roux, A. J. A., and Connell, P. H. Communication No. F(O)1. p. 1 and 3. African regional scientific conference, Johannesburg, South Africa, 1949.

8 British Standards Institution Council for Codes of Practice. "British Standard Code of Practice for Bitumen Felt Roof Coverings." C.P. 144.101, 1952.

9 L'Institut National Technique de L'Étanchéité. "Toitures Terrasses Procédés Multicouches." Paris: INTE, 1949.

10 Building Research Institute. "Roof Decks and Built-Up Roofing." Technical Reprint No. 1, Washington, 1955.

11 Drury, F. E., and Gittins, A. W. "Mastic Asphalt Work." London: Crosby Lockwood & Son Ltd, 1954.

[15] Ballantyne, E. R., and Martin, K. G. CSIRO Div. Build. Res., Building Study No. 1, 1960.
[19] Martin, K. G. CSIRO Div. Build. Res. Tech. Paper No. 8, 1959.
[16] Martin, K. G. CSIRO Div. Build. Res. Tech. Paper No. 11, 1961.
[14] Toch, M. *J. Soc. Chem. Ind.*, 1908, **27**, 311.
[15] Hubbard, P., and Reeve, C. S. *Industr. Engng Chem.*, 1913, **5**, 15.
[17] Reeve, C. S., and Anderton, B. A. *J. Franklin Inst.*, 1916, **182** (4), 463.
[18] Reeve, C. S., and Lewis, R. H. *Industr. Engng Chem.*, 1917, **9**, 743.
[19] Graefe, E. *Asph. u. Teer*, 1932, **32**, 625.
[20] Pfeiffer, J. Ph. *Verfkroniek*, 1935, **8**, 43.
[21] Benson, J. R. *Proc. Highw. Res. Bd, Wash.*, 1937, **17**, 368.
[22] Strieter, O. G. *J. Res. Nat. Bur. Stand.*, 1930, **5**, 247.
[23] Strieter, O. G., and Snoke, H. R. *J. Res. Nat. Bur. Stand.*, 1936, **16**, 481.
[24] Fair, W. F., Beck, H. R., and McKee, B. K. Special Technical Pub. No. 94, p. 109. Philadelphia: ASTM, 1949.
[25] Snoke, H. R., and Gallup, B. E. *J. Res. Nat. Bur. Stand.*, 1937, **18**, 669.
[26] Department of Scientific and Industrial Research. Report of the Building Research Board for the Year 1936. London: HMSO.
[27] Neppe, S. L. *Trans. South African Inst. Civil Engrs*, 1951, **1** (7), 195.
[28] Reinhart, F. W. Special Tech. Pub. No. 236, p. 57. Philadelphia: ASTM, 1958.
[29] Snoke, H. R. *Bull. Amer. Soc. Test. Mat.*, 1957, (220), 41.
[30] Kleinschmidt, L. R., and Snoke, H. R. *J. Res. Nat. Bur. Stand.*, 1959, **63C** (1), 31.
[31] Pfeiffer, J. Ph. "The Properties of Asphaltic Bitumen." Amsterdam: Elsevier, 1950.
[32] Lewis, R. H. *Proc. Ass. Asph. Pav. Tech.*, 1933, **9**, 63.
[33] Mitchell, J. G. *J. Soc. Chem. Ind.*, 1937, **56**, 253T.
[34] Martin, K. G. CSIRO Div. Build. Res. Report 02.5-8, 1960.
[35] Dow, A. W. The reports of the operation of the Engineering Department of the District of Columbia, 1897.
[36] Traxler, R. N., and Schweyer, H. E. *Proc. Amer. Soc. Test. Mat.*, 1936, **36** (Part II), 544.
[37] Traxler, R. N., and Coombs, C. E. *Proc. Amer. Soc. Test. Mat.*, 1937, **37** (Part II), 549.
[38] Lee, A. R., and Markwick, A. H. D. *J. Soc. Chem. Ind.*, 1937, **56**, 146T.
[39] Lee, A. R., and Dickinson, E. J. Road Research Laboratory Tech. Paper No. 31, London: HMSO, 1954.
[40] Dickinson, E. J., and Nicholas, J. H. Road Research Laboratory Tech. Paper No. 16, 1949. London: HMSO.
[41] Dickinson, E. J., Nicholas, J. H., and Boas-Traube, S. *J. Appl. Chem.*, 1958, **8**, 673.
[42] Van Oort, W. P. "A Study of the Aging of Asphaltic Bitumen." Thesis, Delft, 1954.
[43] Van der Poel, C. *J. Appl. Chem.*, 1954, **4**, 221.
[44] Blokker, P. C., and van Hoorn, H. Fifth World Petroleum Congress, 1959, Section VI, Paper 27.
[45] Griffin, R. L., Miles, T. K., and Penther, C. J. *Proc. Ass. Asph. Pav. Tech.*, 1955, **24**, 31.
[46] Thurston, R. R., and Knowles, E. C. *Industr. Engng Chem.*, 1941, **33**, 320.
[47] Hartnell, J. USP 940,808, 23 Nov 1909.
[48] Walther, H. Mitteilungen aus der Dachpappenindustrie, pp 135–52. Berlin: Allgem. Industrie Verlag Knorre and Co., 1938 (*Road Abstract* **5**, No. 611, **6**, No. 477).
[49] Waters, W. A. "The Chemistry of Free Radicals," 2nd Edn. Oxford: Clarendon Press, 1948.
[50] Kennerly, G. W., and Patterson, W. L. *Industr. Engng Chem.*, 1956, **48**, 1917.
[51] Beitchman, B. D. *J. Res. Nat. Bur. Stand*, 1960, **64C**, 13.
[52] Department of Scientific and Industrial Research. "Road Research 1955." London: HMSO, 1956.
[53] Department of Scientific and Industrial Research. "Road Research 1956." London: HMSO, 1957.
[54] Niegowski, S. J. *Industr. Engng Chem.*, 1953, **45**, 632.
[55] Ingold, C. U., and Puddington, I. E. *J. Inst. Petrol.*, 1958, **44**, 168.
[56] Knotnerus, J. *J. Inst. Petrol.*, 1956, **42**, 355.
[57] Goppel, J. M., and Knotnerus, J. *Proc. Fourth World Petrol. Congr.*, 1955, **3**, 399.
[58] Broome, D. C. Paper presented at Second International Mastic Asphalt Conference, Rome, May 1954.
[59] Schriesheim, A., and Greenfeld, S. H. *Bull. Amer. Soc. Test. Mat.*, 1957, (220), 43.
[60] Brooks, B. T., and Humphrey, I. W. *Industr. Engng Chem.*, 1917, **9**, 747.
[61] Bencowitz, I., and Boe, E. S. *Proc. Amer. Soc. Test. Mat.*, 1938, **38**, Part II, 539.
[62] Volkora, V. L. *Antom. Doragi*, 1958, **21** (12), 25. (Road Abstract No. 270, 1959.)
[63] Huet, J. Centre de Recherches Routières, 1958, Rapport de Recherche No. 57/JH/1958.
[64] Brown, A. B., Sparks, J. W., and Larsen, O. *Proc. Ass. Asph. Pav. Tech.*, 1957, **26**, 66.
[65] Greenfield, S. H. National Bureau of Standards, Washington, 1956, Report BMS 147.
[66] Stewart, J. E. *J. Res. Nat. Bur. Stand.*, 1957, **58**, 265.
[67] Beitchman, B. D. *J. Res. Nat. Bur. Stand.* 1959, **63. A**, 189.
[68] Kleinschmidt, L. R., and Greenfeld, S. H. *Bull. Amer. Soc. Test. Mat.*, 1956, **213**, 69.
[69] Corbett, L. W., and Swarbrick, R. E. *Proc. Ass. Asph. Pav. Techn.*, 1958, **27**, 107.
[70] Csanyi, L. H., and Bassi, B. S. *Proc. Ass. Asph. Pav. Techn.*, 1958, **27**, 52.
[71] Chelton, H. M., and Traxler, R. N. Fifth World Petroleum Congress, 1959. Section V, Paper 19.
[72] Fischer, K. A., and Schram, A. Fifth World Petroleum Congress, 1959. Section V, Paper 20.

SOME COMMENTS ON PUMPING REQUIREMENTS FOR NON-NEWTONIAN FLUIDS *

By J. G. SAVINS †

SUMMARY

It is well known that solutions and suspensions of polymeric materials, natural gums, organic soaps, clays, etc., often impart non-Newtonian flow properties to water and hydrocarbons with the result that the laminar flow resistance of these systems is greater than that of the original low viscosity Newtonian medium. Not generally appreciated is that these systems can sustain laminar flow at much higher Reynolds numbers than Newtonian fluids, and when turbulence does develop, the friction factor–Reynolds number correlation lies below that of the conventional turbulent flow correlation, *e.g.* that of Nikuradse, and above an extension of the laminar flow correlation. In certain systems a pronounced diameter effect also occurs. Certain facets of this broad subject area are discussed from the standpoint of their relation to the pumping requirements of these materials, particularly at high Reynolds numbers.

INTRODUCTION

DURING the second world war, studies were made of the problem of increasing the capacity of fuel lines in order to keep abreast of the need for constantly replenishing fuel stocks for highly mobile tactical units. It was found that a pipeline network could be quickly assembled by reeling out flexible pipe from trucks or aircraft. Unfortunately, these were necessarily small diameter lines, and hence their capacities were severely restricted in flow rate because of the high friction losses which arose in turbulent flow.

It was observed that these friction losses could be substantially reduced by adding certain organic gelling agents, *e.g.* aluminium disoaps, to the fuel which was then converted from a thin liquid to a gel-like system. Similar effects were noted in connexion with the development of flame warfare weapons. Some experimental results of wartime studies by Agoston and associates [1] were published in 1954. In one set of experiments, friction losses over the same range of flow rates, in ¼-inch dia tubing, were compared for pure gasoline and for a " 20 gram Gardner " napalm-gasoline gel. Their results are reproduced in Fig 1. Note that the experimental values for the pressure drop in the unthickened gasoline are much higher than those for the gasoline gel. It is estimated that the Reynolds number range for the gasoline is approximately 37,000 to 310,000 in the flow rate range investigated. Even at the lowest flow rate, the thickened gasoline exhibits a lower resistance to flow, while at 10 gal/min the pressure drop of the gel is less than 33 per cent of the pressure drop of the unthickened gasoline. Although the flow of gasoline is definitely turbulent, the authors did not draw any definite conclusions regarding the flow region of the gel. To quote directly from the paper:

> " A less turbulent, more streamlined flow of the jelly could reduce the pressure drop even while the viscosity remains much higher. Whether this is indeed the case, and whether the same paradoxical behaviour is shown by other jellies, remains to be investigated fully."

In 1949 a U.S. patent was issued to Mysels [2] relating to the flow of thickened fluids, more particularly to a method for conveying a liquid such as gasoline through a pipe at high speed. As mentioned above, it had been found that adding a thickening agent capable of

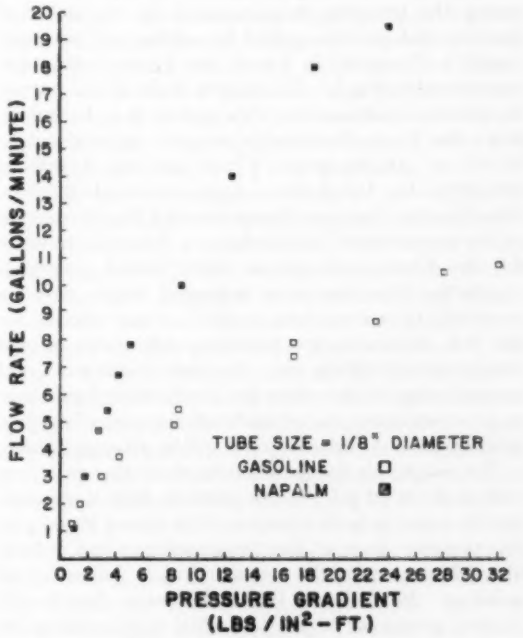
FLOW RATE (GALLONS/MINUTE)
PRESSURE GRADIENT
(LBS / IN2 – FT)
TUBE SIZE = 1/8" DIAMETER
GASOLINE
NAPALM
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20

FIG 1

COMPARISON OF PUMPING REQUIREMENTS FOR GASOLINE AND " 20-GRAM GARDNER " NAPALM GEL

(Data of Agoston, G. A., *et. al.*[1])

* MS received 16 January 1961.

† Socony Mobil Oil Co. Inc., Dallas Texas.

converting gasoline into a gel, *e.g.* napalm agents, lowered the pressure drop below the pressure drop of unthickened gasoline at the same rate of flow. Spectacular reductions in pressure drop were cited, particularly in small diameter tubes. Mysels [2] noted that no theoretical explanation for the effect was available at the time; however, he advanced the theory that the effect was " probably due to the special character of variation of the viscosity coefficient of the *thixotropic* ‡ liquid with rate of shear caused by the flow through the pipe and that the flow of the thickened liquid remains *streamlined and above the rate of flow which causes turbulence* ‡ to a corresponding unthickened Newtonian liquid."

This theory is partly correct in that the effect arises because of the non-Newtonian variable viscosity of the gel; however, as will be shown later, the requirements of conversion to a *thixotropic* gel is not a necessary criterion. Furthermore, it will also be shown that a non-Newtonian system can be flowing at a rate which produces turbulent flow and still exhibit less pressure drop than the unthickened liquid also flowing under turbulent flow conditions.

A portion of the data given in Mysel's patent comparing the pumping requirements for unthickened gasoline and gasoline gelled by adding 4·5 per cent (weight) of napalm in ½-inch and 1-inch tubing are reproduced in Fig 2. The shapes of the Q *v.* J curves for gasoline indicate that this system is in turbulent flow; the Reynolds number range is approximately 35,000 to 141,000 in the ½-inch line and 88,000 to 283,000 in the 1-inch line. Analysis reveals the flow data from the two pipe diameters cited do not coincide on the conventional friction factor v. Reynolds number for the Newtonian system (unthickened gasoline), suggesting the tube sizes indicated might only be nominal; of course there could be other reasons for the lack of coincidence, including differences in pipe roughness, end effects, etc. A similar result was noted on analysing the flow data for the thickened gasoline; as a consequence, no estimate of the prevailing flow conditions on the latter system will be attempted here.

The results for the ½-inch tube show that at a flow rate of about 12 gal/min the pressure drop is approximately equal in both systems, while above 20 gal/min the pressure drop of the thickened gasoline is only about 60 per cent of the pressure drop in the untreated gasoline. In the 1-inch tube the pressure drop is only slightly greater at 60 gal/min, while at 80 gal/min the pressure drop of the thickened gasoline is about 75 per cent of the pressure drop in the untreated gasoline.

These unusual flow effects have also been observed during hydraulic fracturing treatments in oil well drilling operations. Here, the pumping requirement has often been the limiting factor in obtaining high reservoir penetration by means of high fluid injection rates. Studies by Ousterhout [3] indicate that considerable savings in horsepower, *e.g.* friction losses, decreased by as much as 70 per cent, and completions with small diameter casing can be realized by incorporating natural gums and polymers with the injected phase, which take advantage of these unusual turbulent flow effects.

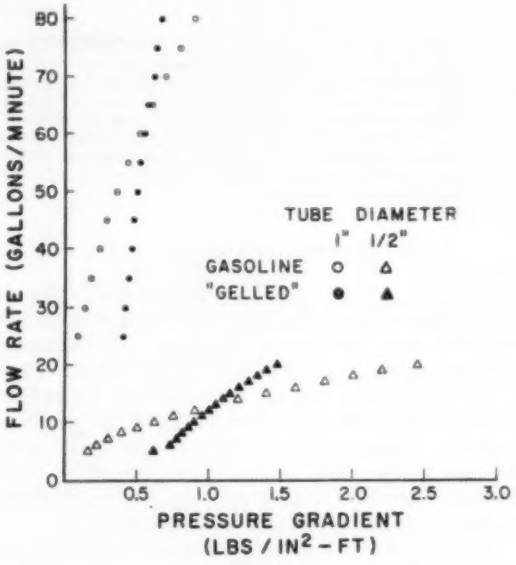

Fig 2

COMPARISON OF PUMPING REQUIREMENTS FOR GASOLINE AND 4·25 PER CENT WT NAPALM IN GASOLINE

(Data of Mysels, K. J.[2])

Similar, but possibly more complicated, behaviour has been observed by Toms [4] in a study of the non-Newtonian system, polymethylmethacrylate–monochlorobenzene, in which a pronounced " diameter effect " occurs only in turbulent flow. These results will be discussed later.

RECENT TURBULENT FLOW CORRELATIONS

Simultaneously in 1959 the results of detailed analysis of turbulent flow in smooth round tubes were published by Shaver and Merrill,[5] and by Dodge and Metzner [6] for a variety of non-Newtonian solutions, gels, and suspensions. These studies indicate that the onset of turbulence occurs at a generalized Reynolds number,[7] *i.e.*

$$N'_{Re} = \frac{D^{n'} V^{2-n'} \rho}{g_c K' (8)^{n'-1}} \equiv \frac{DV\rho}{\mu_A} > 2000 \qquad (1)$$

where V, D, g_c, and μ_A are the bulk average velocity (ft/sec), pipe diameter (ft), a dimensional con-

‡ This author's italics.

version factor, and apparent viscosity defined as $\mu_A = g_c K' D_p^{n'-1}$ respectively. Here n' and K' are the so-called material constants in the power flow law:

$$\tau_p = K'(D_p)^{n'} \quad . \quad . \quad . \quad . \quad (2)$$

where τ_p and D_p are, respectively, the wall shearing stress $\frac{\text{(lb-force)}}{\text{ft}^2}$ and the nominal shear rate (sec^{-1}).

The most interesting result of these studies is that the relationship between the friction factor (f) and N'_{Re} lies below the conventional turbulent flow correlation for viscous Newtonian liquids and above an extension of the laminar curve $f = 16/N'_{Re}$. Furthermore, the relationship between f and N'_{Re} consists of a family of curves which depend on the value of the exponent n' in the power flow law. Fig 3 shows the friction

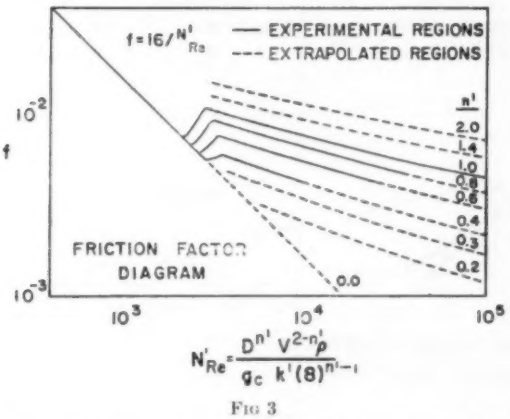

FIG 3

FRICTION FACTOR—REYNOLDS NUMBER CORRELATION FOR TURBULENT FLOW OF NON-NEWTONIAN SYSTEMS

(Data of Dodge, D. W., and Metzner, A. B.[6])

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factor correlations derived by Dodge and Metzner[6]; the plot is essentially the same as that obtained by Shaver and Merrill, the solid lines representing regions in which experimental data were actually obtained.

Dodge and Metzner[6] show by a rather elaborate method that these correlations can be represented by the expression:

$$\frac{1}{\sqrt{f}} = \frac{4{\cdot}0}{(n')^{0.75}} \log_{10}[N'_{Re}(f^{1-n'/2})] - \frac{0{\cdot}40}{(n')^{1.2}} \quad (3)$$

which is a generalization of the well-known turbulence resistance law for Newtonian liquids:[8,9]

$$\frac{1}{\sqrt{f}} = B \log_{10}(N_{Re}\sqrt{f}) - C \quad . \quad . \quad (4)$$

It may be mentioned that the values of B and C determined from Nikuradse's experiments,[10] for example, are about 4·0 and +0·40, respectively. In this regard, Tomita[11] has also generalized equation (4), *i.e.*

$$\frac{1}{\sqrt{f}} = 4{\cdot}06 \log_{10}(N'_{Re}\sqrt{f}) - 0{\cdot}378 \quad . \quad (5)$$

and has satisfactorily correlated pipe flow data for a variety of non-Newtonian material, including starch pastes, lime slurries, etc., using equation (5).

The results shown in Fig 3 illustrate a mechanism by which the friction factor of a low viscosity Newtonian fluid can be reduced at constant flow rate (or the flow rate increased at constant pressure gradient) by the addition of a material which converts the medium to a non-Newtonian solution, gel, or suspension. It is evident, from the positions of the non-Newtonian turbulent flow correlations relative to that of the turbulent flow correlation for Newtonian fluids, that with appropriate combinations of Reynolds number conditions, pipe size, and rheological properties, the situation can arise whereby a friction factor for, say, water, will become higher than that for an aqueous base non-Newtonian system flowing in the same size conduit under identical pumping conditions.

In contrast to the theory advanced by Mysels,[2] these recent correlations indicate reductions in pumping requirements are not necessarily dependent on the formation of a thixotropic gel, but instead are characteristic of a variety of non-Newtonian systems. Such systems can also exhibit the phenomenon of thixotropy, but the latter apparently is not a necessary condition for equation (3) to be applicable.

It has also been suggested that the gel remains in laminar flow while effecting the reduction in pressure loss; this is not necessarily true. The data of Dodge and Metzner[6] indicate the transition from laminar to turbulent flow is shifted to higher values of N'_{Re} as $n' \longrightarrow 0$. As an illustration let $n' = 0{\cdot}30$ for a thickened gasoline and let the flow rate be such that $N'_{Re} = 3200$, *i.e.* the terminus of the $16/N'_{Re}$ line for $n' = 0{\cdot}30$. At the same flow rate the untreated gasoline will very likely be in turbulent flow; hence the thickened gasoline will give a lower pressure drop, since it is still on the $16/N'_{Re}$ line and is flowing under laminar conditions although $N'_{Re} = 3200$. However, according to Fig 3, with further increases in flow rate, *i.e.* for $N'_{Re} > 3200$, the thickened gasoline will deviate from $16/N'_{Re}$ and follow the turbulent correlation for $n' = 0{\cdot}30$. At corresponding flow rates, therefore, both untreated and thickened gasoline will be in turbulent flow, yet from the relative positions of the turbulent correlations it is obvious the pressure drop will be less in the thickened gasoline.

"DIAMETER EFFECTS" IN RELATION TO REDUCED PUMPING REQUIREMENTS

Experiments on a variety of Newtonian liquids in different size tubes show that equation (4) is indepen-

dent of tube diameter, and the data of Dodge and Metzner [6] indicate that equation (3) is also sensibly independent of diameter in the size range ½-inch, 1-inch, and 2-inch for all of the non-Newtonian systems investigated with the exception of a 0·30 per cent (wt) aqueous solution of carboxymethylcellulose. For this system the turbulent correlation falls below the Newtonian curve and does not agree with the appropriate n' value. A pronounced "diameter effect" also results, the friction factors for the three tube sizes being in the order $f_{\frac{1}{2}''} > f_{1''} > f_{1\frac{1}{2}''}$. Furthermore, the laminar curve $f = 16/N'_{Re}$ extends well into the turbulent region, particularly for the ½-inch tube. Dodge and Metzner [6] commented that the limiting viscosity at high shear rates. The author also used the Reynolds group so defined in constructing a friction factor plot for Toms' data. The result of the "diameter-effect" is strikingly illustrated in the conventional correlation between friction factor and Reynolds group given in Fig 4. Note that in the laminar region ($f = 16/Re$), which is the solid line shown, the data on both tube sizes coincide. Only as turbulence develops (at Reynolds numbers between 2000 and 3000) does the "diameter effect" appear, with the result that the friction factors for the polymer solution (closed symbols) all lie below those for the pure solvent (open symbols). Furthermore, in exact analogy to the findings of Dodge and Metzner [6] and

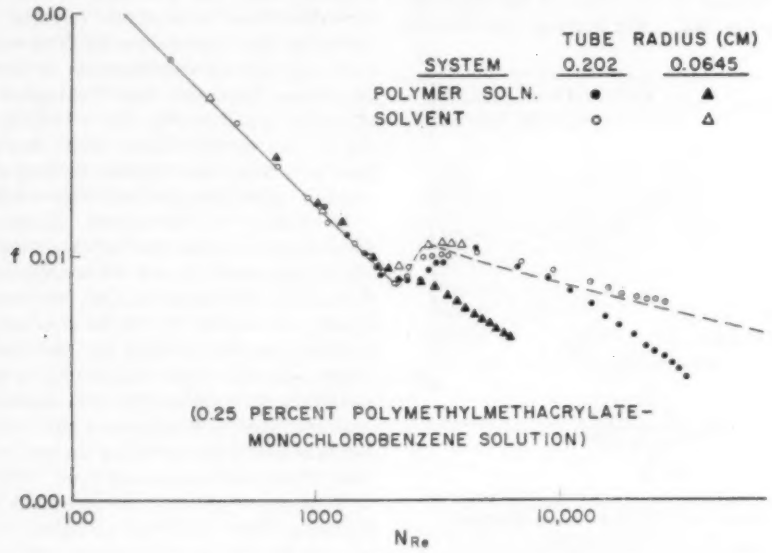

FIG 4

RESULT OF "DIAMETER EFFECT" ON FRICTION FACTOR—REYNOLDS NUMBER CORRELATION
(Data of Toms, B. A.[4])

CMC solutions might "possess some abnormal ability to suppress the formation and propagation of turbulence." The data of Ousterhout [3] also show the "diameter effect," the same trend in friction factor as a function of diameter, and a friction factor correlation less than that predicted from the appropriate n' value.

It occurred to the author that similar behaviour was observed by Toms [4] in connexion with a study of turbulent flow of the system: polymethylmethacrylate–monochlorobenzene, specifically, a 0·25 per cent (wt) polymer solution in cylindrical tubes of radius 0·202 cm and 0·0645 cm, respectively. In this regard, at the time of his study (*ca* 1948) the generalized Reynolds number [7] had not come into use and there was a question as to how the group should be defined for non-Newtonian systems. It was resolved by using Ousterhout,[3] the friction factors are lowest in the small tube. Note that the "diameter effect" is quite pronounced at low turbulent Reynolds numbers in the smaller tube and becomes really significant only at Reynolds numbers in excess of 6000 in the larger tube.

As a check on the effect a Reynolds number based on a limiting viscosity might have on these observations, the author also replotted Toms' data [7] as shearing stress (τ_p) *v.* nominal shear (D_p), as shown in Fig 5. The straight line correlates laminar data points from flow data in both tubes. Note that the transition to turbulence is much more pronounced in the larger tube (circles) than in the smaller tube (triangles) and that both sets of flow data have essentially identical slopes in well developed turbulence. A hint of the surprisingly low viscosity of the polymer solution is shown in the close proximity of both polymer solution and

solvent data points in the laminar region. In this regard, from the straight line was computed $n' = 0.992$ and $K' = 0.0000193 \frac{\text{lb(force)(sec)}^{0.929}}{\text{ft}^2}$. In other words, for all practical purposes $n' \simeq 1$, *i.e.* Newtonian behaviour, yielding a polymer solution viscosity of 0.009 poise, which compares favourably with the limiting viscosity at high shear of 0.0079 poise which Toms [4] reported. Ousterhout [3] also observed very low experimental friction factors in turbulent flow, even at low polymer concentrations where the flow properties were only slightly different from water.

Like the systems studied by Agoston and associates,[1] Shaver and Merrill,[5] and Dodge and Metzner,[6] the mechanism to explain this behaviour. His thesis is based on the presence of an abnormally mobile laminar sub-layer of molecular dimensions near the tube wall when the mainstream is turbulent; this laminar layer arises from the external constraint (and hence preferred direction) the wall presents to the rotational tendencies of a macromolecular structure. An effective velocity of slip (V_s), and a slip coefficient defined as $\xi = V_s/\tau_p$, positive functions of the local conditions of stress at the wall, are introduced on the strength of the argument that, unlike the laminar flow case, the condition of no slip at the wall (in the laminar sub-layer) is not explicitly taken into consideration in the derivation of equation (4). This is taken to mean that

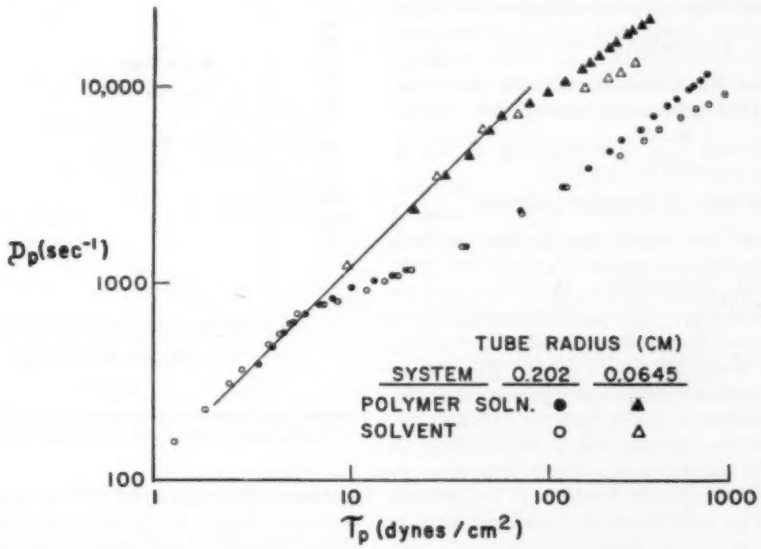

FIG 5

"DIAMETER EFFECT" IN TURBULENT FLOW (0.25 PER CENT POLYMETHYLMETHACRYLATE IN MONOCHLOROBENZENE)
(Data of Toms, B. A.[4])

polymethylmethacrylate–monochlorobenzene system also exhibits a lower friction factor when pumped at the same rate of flow, *e.g.* in the large tube at $N_{Re} = 25{,}000$, $f_{\text{polymer soln}} = 0.61\ f_{\text{solvent}}$. However, the "diameter effect" results in several important differences which should be noted. First, the turbulent flow correlations in Fig 4 are seen to yield friction factors much lower than would be predicted for the same Reynolds numbers and the appropriate value of $n' = 0.992$ from Fig 3. Secondly, the reduction in pumping requirement occurred only in turbulent flow. Similar effects reported by Dodge and Metzner [6] for CMC solution and by Ousterhout [3] have been attributed to the presence of viscoelasticity in these systems, the elasticity tending to suppress the appearance of turbulent eddies.

Oldroyd [12] has suggested a somewhat different the only effect V_s in the laminar layer has on the velocity distribution in turbulent flow is to superpose upon it a uniform velocity in the direction of flow. Substituting $V - V_s$ in the derivation of equation (4), Oldroyd [12] obtains:

$$\frac{1}{\sqrt{f}} = B \log_{10}(N_{Re}\sqrt{f}) - C + \tfrac{1}{2}\left(\frac{\xi_\eta N_{Re}\sqrt{f}}{D}\right) \quad (6a)$$

which can also be written as:

$$\frac{1}{\sqrt{f}} = B \log_{10}(N_{Re}\sqrt{f}) - C + \left(\frac{V_s}{V}\frac{1}{\sqrt{f}}\right) \quad (6b)$$

The principal result of this modification of equation (4) is to produce a striking divergence in the friction factor correlation when $\frac{D}{2}$ is of the order of $\xi\eta$, which is exactly the same as that shown in Fig 4 and also

reported by Dodge and Metzner [6] and Ousterhout.[3] It should also be noted that the divergence is shifted to progressively higher Reynolds numbers as the tube diameter is increased. This also agrees with these data.

SOME PREDICTIONS CONCERNING PUMPING REQUIREMENTS

It is worthwhile to present some calculations of the magnitude of the friction loss reduction which might be predicted from these correlations for various flow rate conditions. The influence of non-Newtonian flow characteristics on pumping requirements is illustrated on comparing a set of laminar-turbulent flow curves for water and a system comprised of water and a thickener. For water $\left(\eta = 0{\cdot}000672 \frac{\text{lb-mass}}{\text{ft-sec}}\right)$ while for the non-Newtonian system the following properties have been arbitrarily selected: $n' = 0{\cdot}30$, $K' = 0{\cdot}003$ lb (force) $\frac{\text{sec}^{0{\cdot}3}}{\text{ft}^2}$; multiplying K' by g_c yields a pseudoviscosity of the order of $0{\cdot}0966 \frac{\text{lb-mass}}{\text{ft-sec}^{1{\cdot}7}}$

For convenience the results are plotted on both cartesian and logarithmic scales, Fig 6 (*a*) and 6 (*b*) respectively. The calculated flow data shown are for 3·826-inch diameter pipe. The turbulent curve shown for water is derived from the conventional $f - N_{Re}$ diagram for flow in smooth round tubes. The transition regions for both materials are represented in Fig 6 (*b*) by discontinuities in the flow curves. For water, the terminus of the laminar curve corresponds to $N_{Re} = 2000$ with the turbulent curve beginning at $N_{Re} = 3000$. For the gel, the terminus of the laminar curve occurs at $N'_{Re} = 3200$ and the turbulent curve is shown beginning at $N'_{Re} = 4000$.

These data show that below $N_{Re} \cong 39{,}000$ the pressure drop in the gel is considerably greater than the drop in the water system at equivalent flow rates. Note the relative insensitivity to flow rate in the gel system below $N'_{Re} = 3200$, Fig 6 (*b*), especially. Aside from the attractive possibility that the capacity of a pumping system for a non-Newtonian material may be increased simply by speeding up the pump, because of this flow rate insensitivity, this effect accounts for some of the difficulties in metering non-Newtonian materials by means of a flowmeter which operates

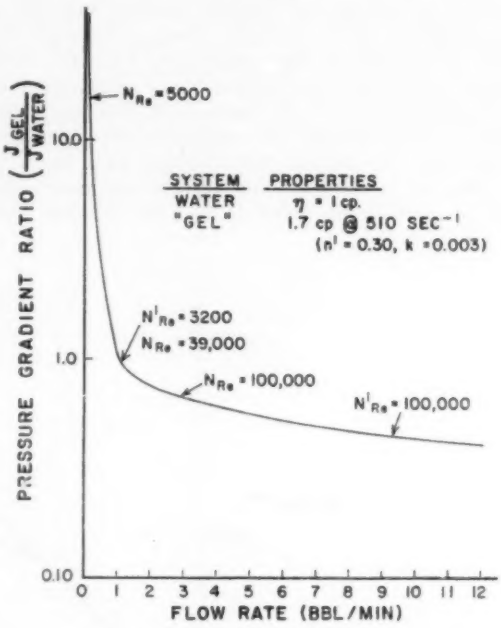

Fig 6 (*a*)

COMPARISON OF PREDICTED PUMPING REQUIREMENTS FOR WATER AND "GEL" IN LAMINAR-TURBULENT REGIONS

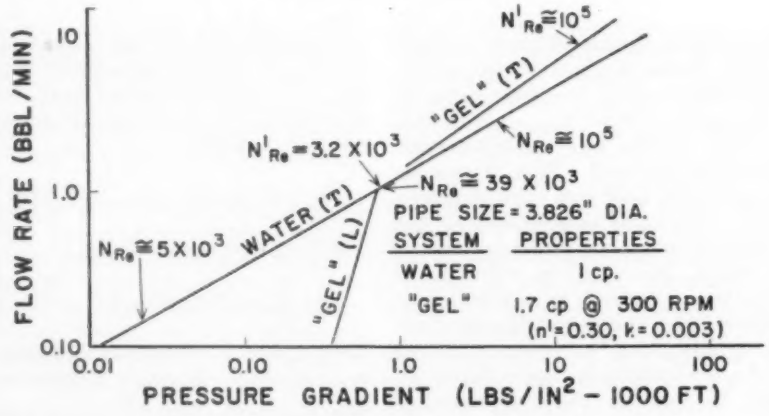

Fig 6 (*b*)

COMPARISON OF PREDICTED PUMPING REQUIREMENTS FOR WATER AND "GEL" IN LAMINAR-TURBULENT REGIONS

under a feedback action derived from monitoring the pressure gradient.[13]

At a flow rate of *ca* 1 brl/min, the pressure gradient characteristics of the gel are more favourable than those of the water system, with spectacular reductions in pressure drop occurring for moderate increases in

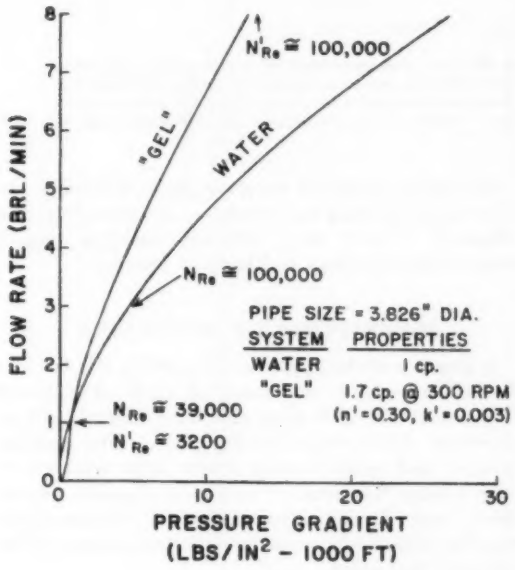

Fig 7

PREDICTED EFFECT OF FLOW RATE ON PRESSURE GRADIENT RATIO IN 3·826-INCH DIAMETER PIPE

flow rate as shown in Fig 7, a plot of the pressure gradient ratio $\frac{J \text{ gel}}{(J \text{ water})}$ *v.* flow rate. These data show that a flow rate of 1·5 brl/min the pressure gradient of the gel is 83 per cent of the pressure gradient of water, at 5 brl/min it has decreased to 56 per cent, and at 10 brl/min the reduction is *ca* 44 per cent. In this regard, calculations predict that the pressure drop reduction will be even more striking in small diameter tubing, a fact which has been substantiated by prior studies reviewed here.

CONCLUSIONS

The fact that non-Newtonian fluids can sustain laminar flow at much higher Reynolds numbers and exhibit a lower degree of agitation when turbulent flow does develop has important implications in establishing the optimum pumping requirements for solutions and suspensions consisting of water or hydrocarbons and polymeric materials, natural gums, organic soaps, clays, etc. The review presented here of some of the facets of this broad subject area suggests an explanation for what is regarded as a paradox in certain applications, namely, the observation that the pumpability of a low viscosity Newtonian medium at constant pressure gradient can be significantly increased (or the pressure gradient decreased at constant flow rate) for certain combinations of Reynolds numbers and conduit diameters, on the addition of certain agents which tend to thicken or gel and impart non-Newtonian rheological properties to the medium.

ACKNOWLEDGMENT

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References

1 Agoston, G. A., *et al.* *Industr. Engng Chem.*, 1954, **46**, 1017.
2 Mysels, K. J. U.S.P. 2,492,173.
3 Ousterhout, R. S., and Hall, C. D., Jr. Paper No. 1596-G presented at the 35th Annual Fall Meeting, SPE-AIMME, Denver, Colorado, 2–5 Oct 1960.
4 Toms, B. A. "Proceedings International Rheological Congress, Holland (1948)." Amsterdam: North Holland Publishing Co., 1949.
5 Shaver, R. G., and Merrill, E. W. *J. Amer. Inst. Chem. Engrs*, 1959, **5**, 181.
6 Dodge, D. W., and Metzner, A. B. *J. Amer. Inst. Chem. Engrs*, 1959, **5**, 189.
7 Metzner, A. B., and Reed, J. C. *J. Amer. Inst. Chem. Engrs*, 1955, **1**, 434.
8 Schlichting, H. "Boundary Layer Theory." New York: McGraw-Hill, 1955.
9 von Karman, Th. National Advisory Committee for Aeronautics, Technical Memo. No. 611 (1931), Washington, D.C.
10 Nikuradse, J. *VDI Forsch. heft*, 1932, 356.
11 Tomita, V. *Bull. JSME*, 1959, **2**, 10.
12 Oldroyd, J. G. "Proceedings International Rheological Congress, Holland (1948)." Amsterdam: North Holland Publishing Co., 1949.
13 Head V. D. *TAPPI*, 1952, **35**, 260.

THE EFFECT OF PRE-FLOODING ON PACKED DISTILLATION COLUMNS *

By K. E. PORTER † and J. VARJAVANDI †

SUMMARY

The effect of pre-flooding on hold-up, pressure drop, and efficiency was measured for ¼-inch ceramic Raschig rings and Multifill packing. Pre-flooding was shown to have no effect on the performance of the Multifill packing. The hold-up and pressure drop of the Raschig rings were found to increase with pre-flooding for pure solvents but not for the binary mixture methyl*cyclo*hexane–*n*-heptane. However, the efficiency of the Raschig rings in separating the binary mixture did increase.

INTRODUCTION

PRE-FLOODING a packed distillation column is the process of starting a distillation by increasing the boil-up rate until the column floods and then slowly decreasing the boil-up rate until flooding subsides. Normal steady operation is then continued.

It is generally accepted that pre-flooding results in higher rates of mass transfer in packed columns. However, an investigation of the literature shows few results on the quantitative effect of pre-flooding. An extensive investigation by Fenske and co-workers [1–3] on the efficiency of different packings showed that in many cases the efficiency of the column was improved by pre-flooding. They suggested that this was due to surface tension effects which caused the condensate to form drops or rivulets on a dry packing but spread uniformly on a wet one. A close inspection of their results shows that higher efficiencies are obtained by pre-flooding only when porous packing is used. On the other hand, Carney [4] states that the increase of efficiency with pre-flooding is a characteristic of metal packings; a preliminary film of liquid on the packing is necessary to obtain a uniform flow and even distribution or reflux. The high efficiency of Dixon wire gauze rings [5] depends on an elaborate pre-flooding technique.

Hayter [6] claims that the performance of doubly corrugated gauze packings is unaltered by pre-flooding owing to the numerous capillary passages of the packing which distribute the liquid. Multifill packing developed by Goodloe,[7] and claimed to be self-wetting, consists of a fabric of knitted strands, each strand consisting of several wire filaments. Strong capillary distribution along the strands may be expected.

If a gain in efficiency of a packing caused by pre-flooding is due to increased wetting it may be accompanied by a gain in liquid hold-up and an increase in pressure drop across the packing. These effects of pre-flooding have received little or no previous attention.

This paper describes experiments to determine the effect of pre-flooding on the hold-up, pressure drop, and efficiency of two very different packings, ¼-inch ceramic Raschig rings and Multifill packing.

DESCRIPTION OF APPARATUS

A diagram of the apparatus is given in Fig 1. The distillation column was made of 12 ft of standard 2-inch diameter QVF glass pipe in two equal sections separated by a redistributing plate. The packing support and redistributing plates were designed to offer a large free area by means of separate vapour risers and liquid downcomers. A thermocouple inserted at each plate measured the temperature of the reflux at that point.

The column was jacketed by two standard QVF glass pipes of 3 inches diameter, and near adiabatic operation was obtained by circulating a heated glycerine–water mixture through the annulus formed. The temperature of the circulating liquids was checked at six different points in the circuit by means of thermocouples, and maintained constant within ±0·1° C by means of a constant temperature bath. Vapours from the column were condensed in a 2-inch diameter by 2-ft long glass multicoil condenser having a total area of 3·5 sq ft. The condensate was made to flow through a modified burette prior to entering the packed section, and the reflux rate was measured from the liquid level in the burette. This rate meter had been previously calibrated. The rate was also calculated from the heat balance, and the two values agreed favourably.

The re-boiler was made from a 12-inch long, 8-inch diameter standard copper pipe with both ends blanked with ¼-inch thick copper sheet. Copper was chosen for the reboiler since it did not react with the *o*-phenanthroline which was used in the hold-up measurements.

The re-boiler was heated by two separate 1-kw elements strapped externally round the lower circumference of the re-boiler and by two separate 500-watt

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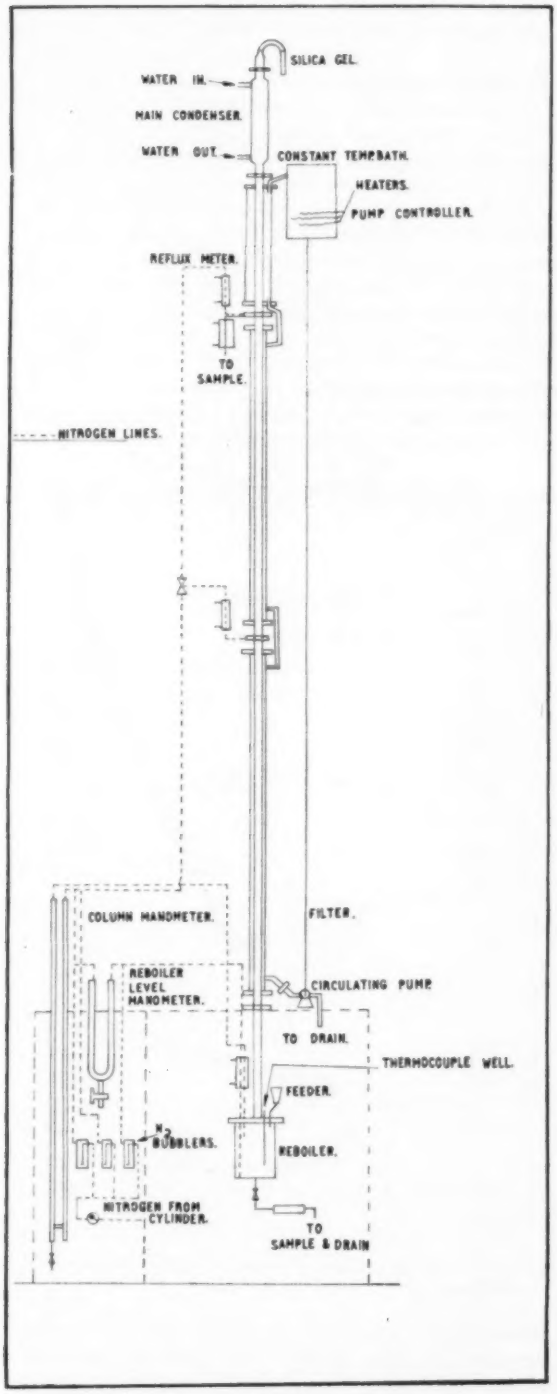

FIG 1
PACKED DISTILLATION COLUMN

heaters clamped to the bottom of the re-boiler and each controlled by a "Variac" auto-transformer. The re-boiler was lagged by 2-inch thick asbestos lagging. As some of the hold-up measurements were determined by measuring the change in the level of the liquid in the re-boiler, this influenced its shape and size.

Pressure tappings were provided in the brass plates at each end of the packed sections. A continuous bleed of nitrogen was passed through the pressure transmitting lines to prevent errors due to condensation of vapour in the lines, and this small flow of nitrogen through the lines was regulated by its rate of bubbling through glass oil bubblers. Entry of condensable vapour into the lines was also prevented by the small condensers in the nitrogen lines shown in the diagram. The pressure drop across the column was recorded by a 5-ft long water manometer, and a smaller kerosine manometer indicated the level of liquid in the still.

DETERMINATION OF HOLD-UP

In order to keep the temperature and the physical properties of the phases constant throughout the packing, both before and after pre-flooding, pure solvents were used in the hold-up and pressure drop experiments.

The total hold-up in the column was found from the change in volume of the liquid in the still. With the column packed with Raschig rings this was found from the change in concentration of the non-volatile substance *o*-phenanthroline $C_{12}H_8N_2$, which was added to the liquid in the still. This method is similar to that of Fenske,[1] who used stearic acid as the non-volatile substances. *o*-Phenanthroline is a very stable molecule in crystalline form which is soluble in the solvents used in this work. It has the advantages that only a trace of it is required and a small sample is easily and accurately analysed by a spectrophotometer. It is, however, necessary to calibrate "percentage of light transmitted" against "concentration of *o*-phenanthroline" in the solvent under investigation, and since the calibrations are different for different solvents, the method may be used only to determine the hold-up of a pure solvent and not for a mixture of solvents. Full details of this method have been given.[8]

This method of analysis was sufficiently accurate to allow determination of the vapour losses into the small continuous nitrogen bleed from the pressure tappings. Vapour losses appear as an apparent small increase in hold-up with time, while boil-up rate and pressure drop remained constant. The results of a determination of vapour losses is shown in Fig 2. These losses amounted to 6·5 ml/hr for carbon tetrachloride and 9 ml/hr for methyl alcohol. They depended only on the nitrogen flow. This was kept constant, and the

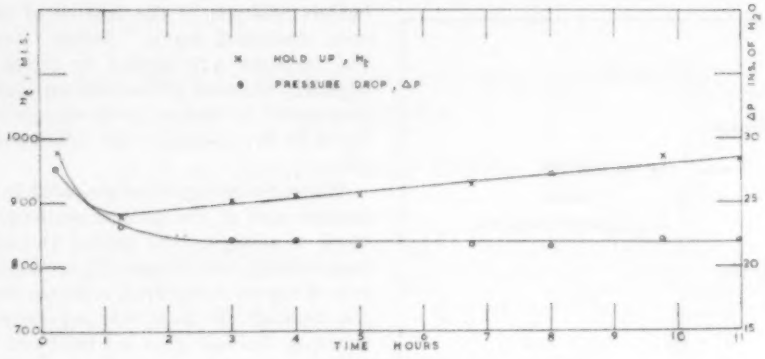

FIG 2

ESTIMATION OF VAPOUR LOSSES FOR METHYL ALCOHOL

corresponding corrections were made to the hold-up determinations.

It was found impossible to use the *o*-phenanthroline method for hold-up determinations with Knitmesh Multifill. This packing was supplied by the manufacturers coated with preservatives, and difficulties were encountered in cleaning the packing. The packing was washed by re-fluxing the column for several hours using each of the following solvents: methyl alcohol, acetone, and carbon tetrachloride. Nevertheless, the samples taken from the re-boiler were highly coloured due to the complex reactions of *o*-phenanthroline.

In the tests on the Multifill packing the change in volume of the still liquid was found by direct measurement of the liquid level by means of the manometer. This method enabled a change in volume of the still liquid of less than 50 ml to be detected, which represented a column hold-up of 0·01 ml/ml.

PROCEDURE

The solvents used in the different experiments are given in Table I. All tests were at total reflux.

TABLE I

Solvents Used in Experiments

Experiment	¼-inch Raschig rings	Knitmesh Multifill
Hold-up	Methanol Carbon tetrachloride	Methanol Carbon tetrachloride
Pressure drop	Methanol Acetone Carbon tetrachloride *n*-Heptane-methyl-*cyclo*hexane	Methanol Acetone Carbon tetrachloride Methyl*cyclo*hexane–*n*-heptane
Efficiency	Methyl*cyclo*hexane–*n*-heptane	Methyl*cyclo*hexane–*n*-heptane

The column and still were washed with a solvent (usually acetone) and dried thoroughly with com-

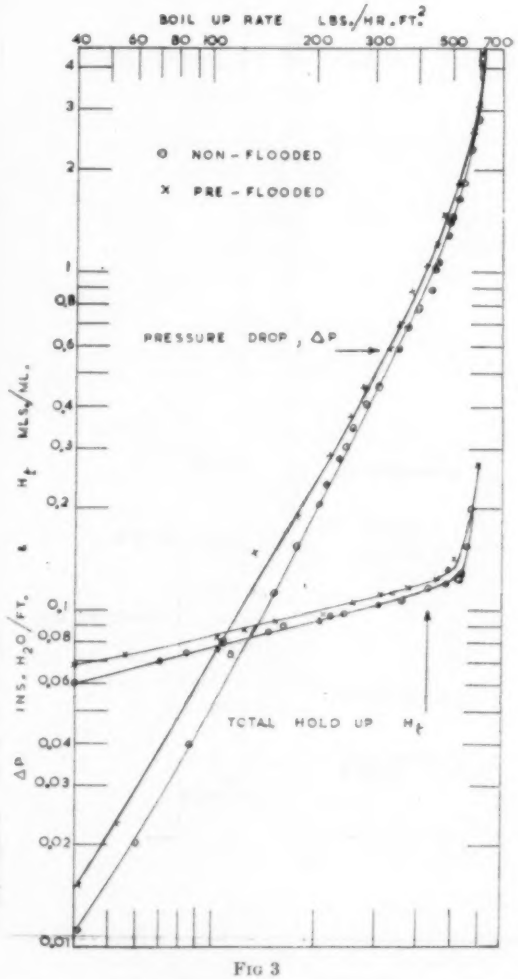
BOIL UP RATE LBS./HR.FT.^{2}
40 60 80 100 200 300 500 700
○ NON-FLOODED
× PRE-FLOODED
PRESSURE DROP, ΔP
TOTAL HOLD UP H_t
H_t MLS./ML.
ΔP INS. H_2O/FT.
4 3 2 1 0.8 0.6 0.4 0.3 0.2 0.1 0.08 0.06 0.04 0.03 0.02 0.01

FIG 3

HOLD-UP AND PRESSURE DROP FOR METHANOL IN ¼-INCH RASCHIG RING COLUMN

pressed air prior to each run. The jacket circulating system was adjusted to the correct temperature before the column was started up.

In the hold-up and pressure drop determinations the re-boiler was charged with 2·5 l of liquid and approximately 0·1 g of *o*-phenanthroline crystals weighed to the nearest hundredth of a milligram. For non-flooded runs the column was maintained at the minimum boil-up rate for a period of not less than 2 hours, to allow the apparatus to reach temperature equilibrium. The temperatures at the top and bottom of the column, the jacket temperature, the reflux rate, and the liquid level in the re-boiler were recorded together with heat input into the re-boiler and column pressure drop. A 10-ml sample from the re-boiler liquid was also taken for hold-up estimations. The heat input into the re-boiler was increased gradually every hour and the above readings and a sample were

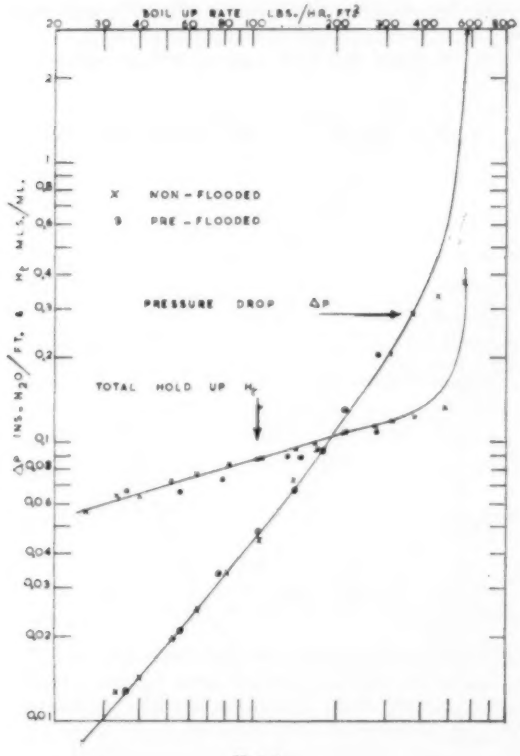

FIG 4

HOLD-UP AND PRESSURE DROP FOR METHANOL IN MULTIFILL PACKED COLUMN

taken. It was shown by preliminary experiments that pressure drop and hold-up remained constant after a period of 30–45 minutes, depending on the boil-up rate.

The pre-flooded runs were done after flooding the column for a period of 30 minutes. At these flooding velocities the pressure drop across the packings was about 60 inches of water for the Raschig rings, and about 30 inches of water for the Multifill packing.

The boil-up rate was then reduced gradually every hour and the readings and sample taken as in the pre-flooded runs.

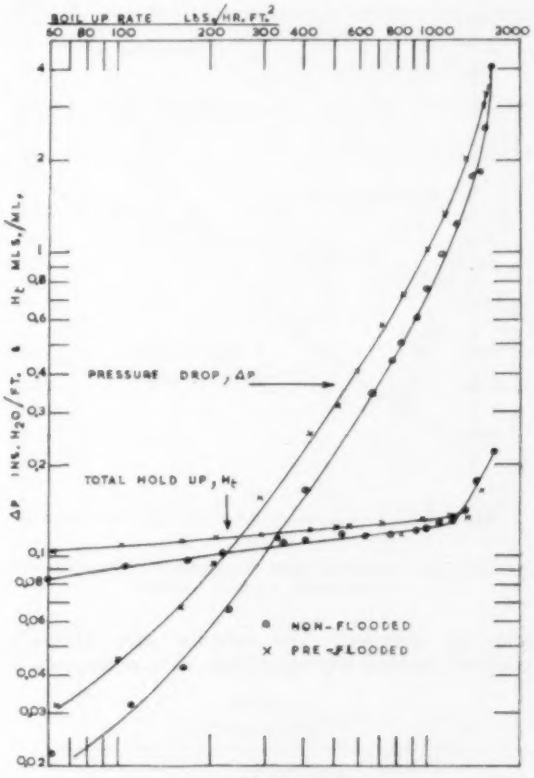

FIG 5

HOLD-UP AND PRESSURE DROP FOR CARBON TETRACHLORIDE IN ¼-INCH RASCHIG RING PACKED COLUMN

Each set of curves was not necessarily obtained in a continuous run. It was found that there was no break or discontinuity in the data when obtained during several different runs, and each point could be satisfactorily duplicated.

Both pre-flooded and non-flooded efficiency runs were carried out, the procedure being somewhat similar to the hold-up and pressure drop runs described above. The system used was *n*-heptane–methyl*cyclo*hexane and the samples were analysed by a Zeiss–Abbé refractometer. Vapour–liquid equilibria data and refractive index data were obtained from Bromiley and Quiggle.[9] A period of 2½ hours proved sufficient for the column to reach equilibrium at each boil-up rate. 5-ml samples were taken from the top of the column and from the re-boiler, the samplers being flushed with approximately 10 ml of the liquid

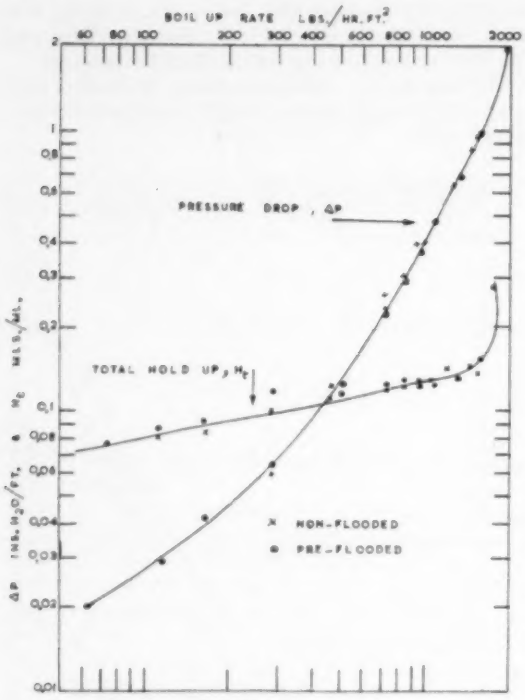

FIG 6

HOLD-UP AND PRESSURE DROP FOR CARBON TETRACHLORIDE IN MULTIFILL PACKED COLUMN

prior to sampling. The samples were normally analysed immediately after they were taken, but in some cases they were kept in a refrigerator until they were analysed. Pressure drop readings for the binary mixture were also recorded.

TABLE II

Packing Properties

Packing	Surface area, ft²/ft³	Voidage fraction	Material of construction	Size	Other information
Raschig rings	242	0·625	Porcelain	½ inch	
Multifill	600	0·95	Copper	—	8 filaments of 0·0048 inch wire per strand, knitted to form a fabric 4 inches wide. Crimped at 45°, crimps ⅜ inch apart

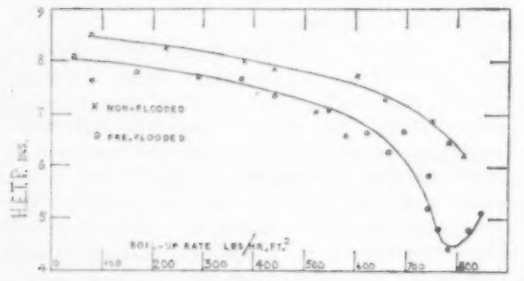

FIG 7

EFFICIENCY RESULTS FOR ½-INCH RASCHIG RINGS SYSTEM *n*-HEPTANE–METHYL*cyclo*HEXANE

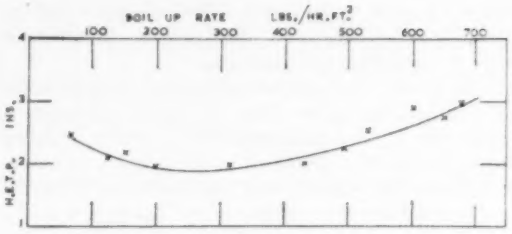

FIG 8

EFFICIENCY RESULTS FOR MULTIFILL SYSTEM *n*-HEPTANE–METHYL*cyclo*HEXANE

EXPERIMENTAL RESULTS

Figs 3–9 illustrate the different effect of pre-flooding on ½-inch Raschig rings and Multifill packing.

For the rings, for both hold-up and pressure drop

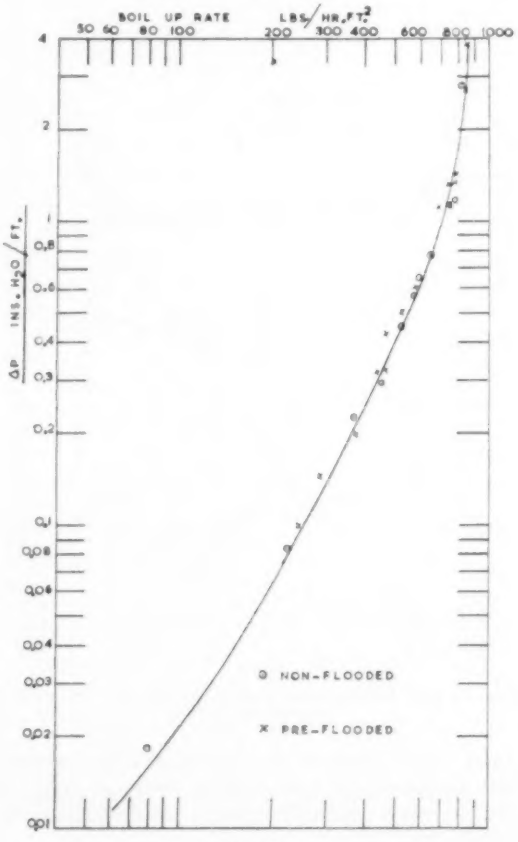

FIG 9

PRESSURE DROP RESULTS FOR *n*-HEPTANE–METHYL*cyclo*HEXANE IN RASCHIG RING COLUMN

two separate curves were obtained for the pure solvents, the pre-flooded curve in each case being higher than the non-flooded. For the Multifill packing no difference was found between pre-flooded and non-flooded runs, all the results lying apparently on the same curve. These differences in the effect of pre-flooding on the packings suggest that pre-flooding increases the wetted area of the Raschig rings, but not that of the Multifill packing, which is probably wet by capillary action along the strands rather than by a liquid film over its surface.

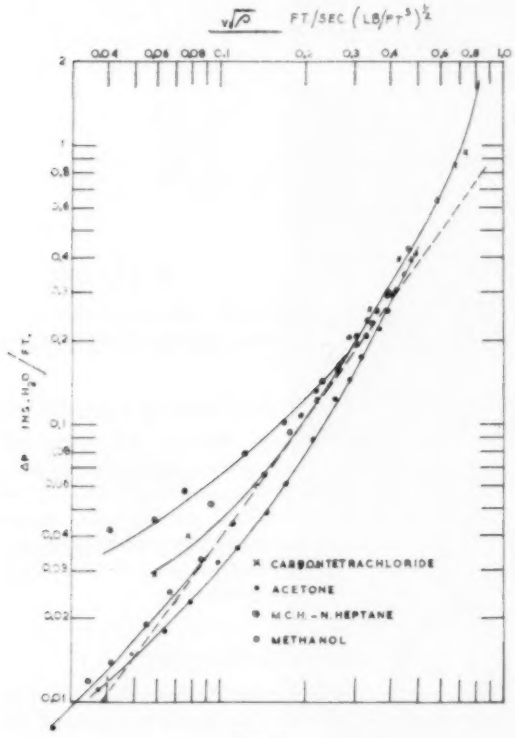

FIG 10

CORRELATION OF PRESSURE DROP THROUGH MULTIFILL PACKED COLUMN BY METHOD OF REED AND FENSKE

It was expected that the pressure drop results at different boil-up rates for the binary system *n*-heptane–methyl*cyclo*hexane would show similar differences between pre-flooded and non-flooded runs for ¾-inch Raschig rings. However, all the results were found to lie on one curve, Fig 9.

This is probably due to the fact that for the *n*-heptane–methyl*cyclo*hexane system the reflux has a positive surface tension change down the column such that the Maragnoni effect may give complete wetting of the packing even under non-flooded conditions.[10] The gain in efficiency of the Raschig rings by pre-flooding may be due to more effective irrigation of the completely wetted packing. In other words, pre-flooding may tend to remove those relatively stagnant areas of wetted packing surface. The efficiency of the Multifill packing remains unchanged by pre-flooding.

The experiments described above were designed to gain further insight into the phenomena of pre-flooding, and the results obtained are insufficient to attempt a general correlation of pressure drop and hold-up. Comparisons were made between the experi-

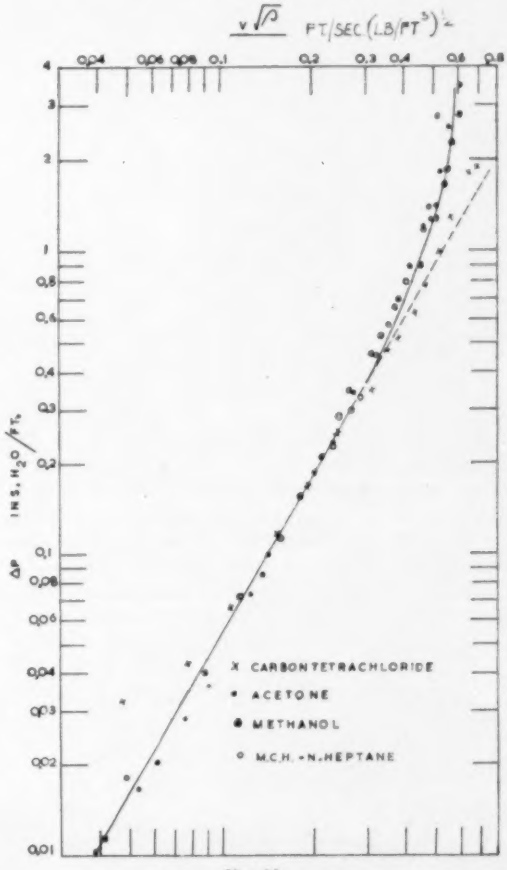

FIG 11

CORRELATION OF PRESSURE DROP THROUGH RASCHIG RING PACKED COLUMN BY METHOD OF REED AND FENSKE

mental results and the predictions of methods given in the literature for Raschig rings.

It was found that the pressure drop results were best correlated by the method of Reed and Fenske [11] of plotting the pressure drop against $v\sqrt{\rho_g}$. This is shown in Fig 11 for Raschig rings and in Fig 10 for the Multifill packing.

When total hold-up was plotted against boil-up rate on logarithmic co-ordinates, straight line relationships were found up to flooding. The slope of the curves turned almost vertically upward at the flooding point, Figs 3 and 5. The total hold-up at the flooding point

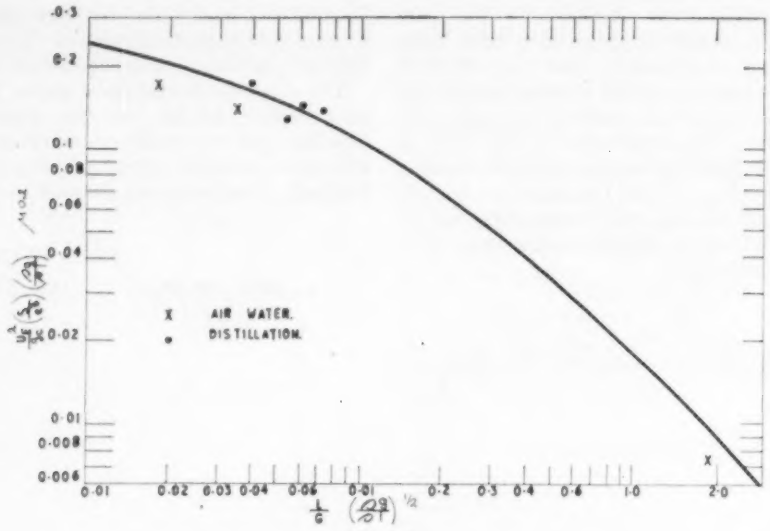

FIG 12

FLOODING VELOCITY CORRELATION

was the same for both methanol and carbon tetrachloride.

No apparent break in the hold-up curve below flooding occurred to indicate a loading point. This break has been reported by some previous investigators [12] and is used to explain the mechanism of loading.

The flooding velocities in the Raschig ring packed column were correlated by the method of Sherwood, Shipley, and Holloway.[13] The results are given in Table III and presented in Fig 12. Fig 12 shows that

TABLE III

Application of Sherwood's[13] Flooding Correlation

$S = 242$ sq ft/cu ft $\quad \epsilon = 0{\cdot}625 \quad \therefore S/\epsilon^3 = 1000$

Systems	G_F, lb/hr ft²	U_F, ft/sec	g/l	$1^{0{\cdot}5}$	B	A
Methyl alcohol	530	2·035	0·00155	0·807	0·0394	0·172
Acetone	650	1·350	0·00287	0·746	0·0529	0·125
Carbon tetrachloride	1500	1·200	0·00374	0·874	0·0611	0·143
Methylcyclohexane–n-heptane	800	1·084	0·00526	0·728	0·0725	0·138
Air–water	390	1·34	0·00129	1·000	1·8100	0·072
	540	1·86	0·00129	1·000	0·0359	0·139
	600	2·06	0·00129	1·000	0·0179	0·170

$$\frac{U_F^2 \rho_g S}{g_c \epsilon^3}\left(\frac{}{\rho_l}\right)\mu_l^{0{\cdot}2} = \phi\left[\frac{L}{G}\left(\frac{\rho_g}{\rho_l}\right)^{\frac{1}{2}}\right]$$

$$A = \phi[B]$$

Symbols

ϵ	voidage fraction of packing	U_F	gas velocity at flooding point
g_c	gravitational constant	v	gas velocity
G	gas mass velocity	ρ_g	density of gas
L	liquid mass velocity	ρ_l	density of liquid
S	specific surface of packing	μ_l	viscosity of liquid

the results agree quite well with the correlation. Also presented are the results of some air–water experiments with the Raschig ring column; these are also in agreement with the correlation.

These results confirm that the Sherwood correlation, originally developed for air–water and absorption systems, may also be used satisfactorily for distillation.

CONCLUSION

This investigation shows that for ¼-inch ceramic Raschig rings, pre-flooding gives a higher efficiency for the system, methyl*cyclo*hexane–*n*-heptane, and for the pure components methyl alcohol and carbon tetrachloride a higher pressure drop and hold-up.

For the self-wetting Multifill packing, pressure drop, hold-up, and efficiency are unaltered.

ACKNOWLEDGMENT

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References

1. Fenske, M. R. *Industr. Engng Chem.*, 1934, **26**, 1213.
2. Fenske, M. R., Tongberg, C. O., and Quiggle, D. *Industr. Engng Chem.*, 1934, **26**, 1169.
3. Fenske, M. R., Lawroski, S., and Tongberg, C. O. *Industr. Engng Chem.*, 1937, **29**, 957; 1938, **30**, 293.
4. Carney, T. P. "Laboratory Fractional Distillation." New York: The Macmillan Co., 1949.
5. Dixon, O. G. *J. Soc. Chem. Ind.*, 1949, **68**, 88.
6. Hayter, A. J. *Ind. Chem.*, 1952, **28**, 59.
7. Bragg, L. B. *Industr. Engng Chem.*, 1957, **49**, 1062.
8. Varjavandi, J. Ph.D. Thesis, Univ. of Birmingham, 1959.
9. Bromiley, E. C., and Quiggle, D. *Industr. Engng Chem.*, 1933, **25**, 1136.
10. Zuiderweg, F. J., and Harmens, A. *Chem. Engng Sci.*, 1958, **9**, 89.
11. Reed, T. M., and Fenske, M. R. *Industr. Engng Chem.*, 1950, **42**, 654.
12. Shulman, H. L., *et al.* *J. Amer. Inst. Chem. Engrs*, 1955, **1**, 253.
13. Sherwood, T. K., Shipley, G. H., and Holloway, F. A. L. *Industr. Engng Chem.*, 1938, **30**, 765.

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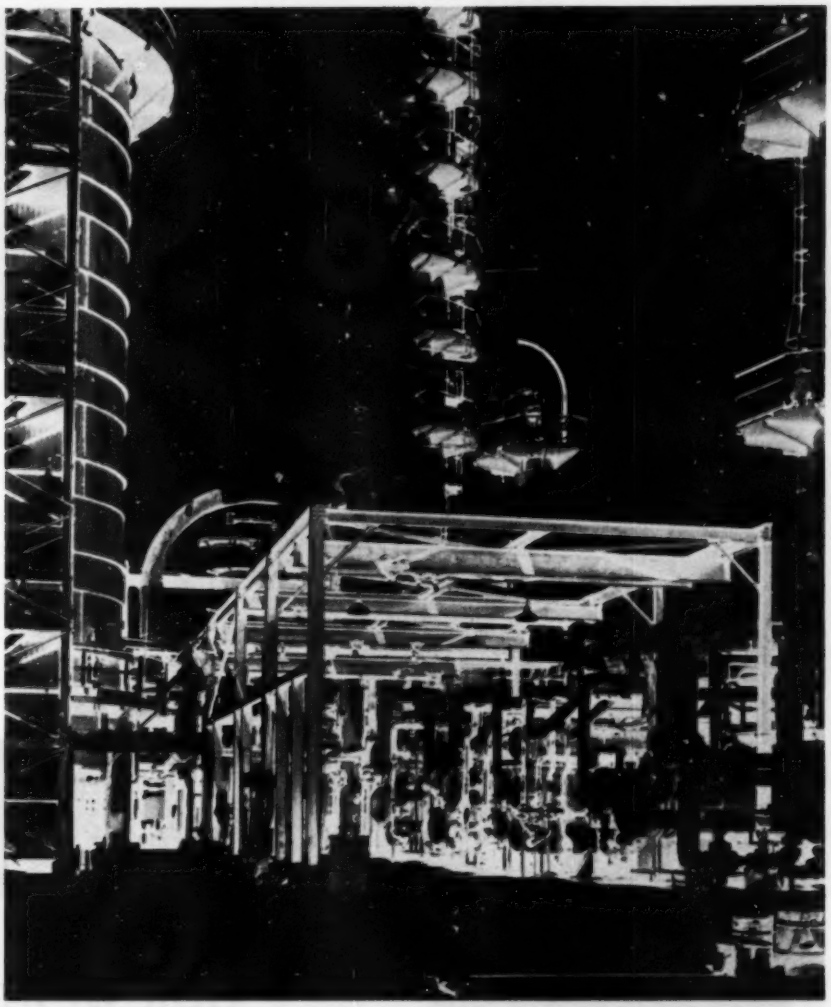

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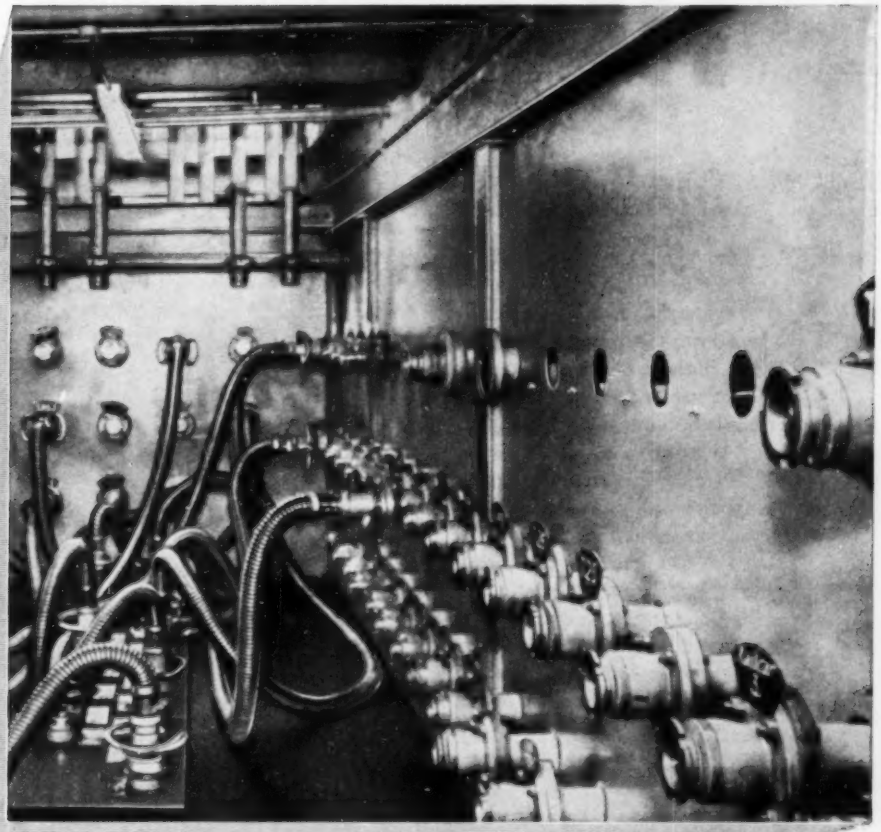

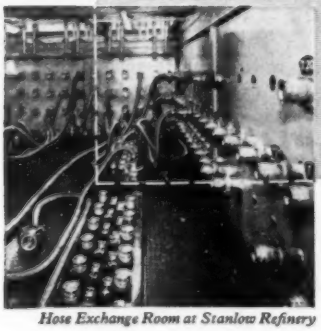

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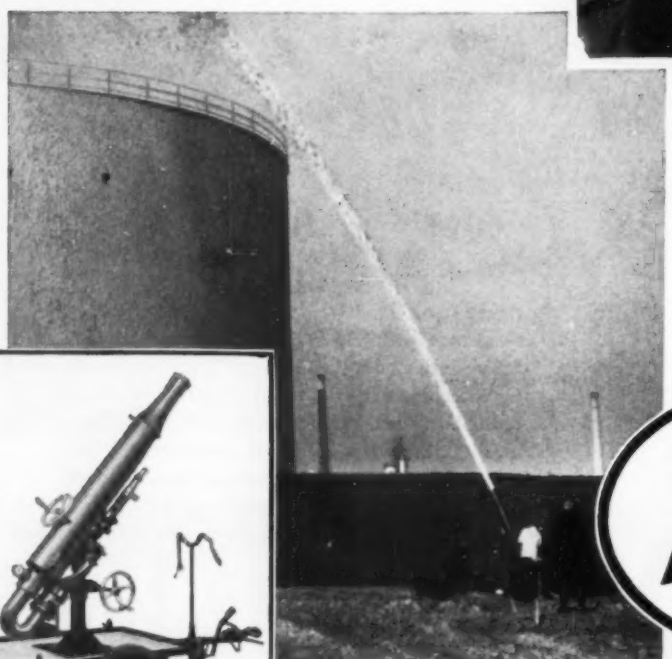

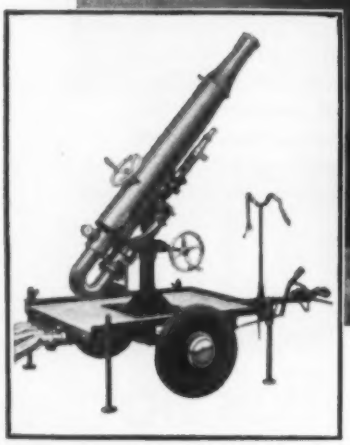

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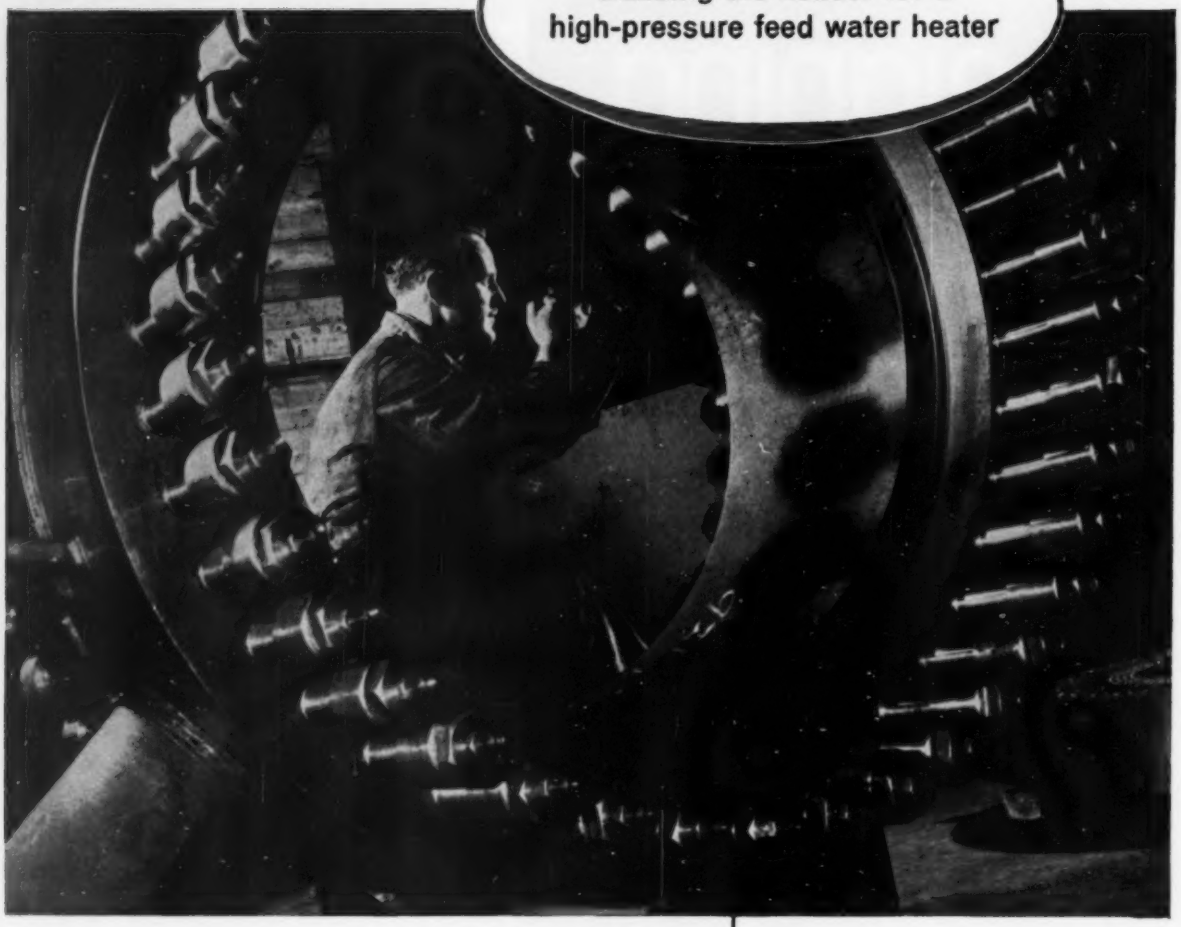

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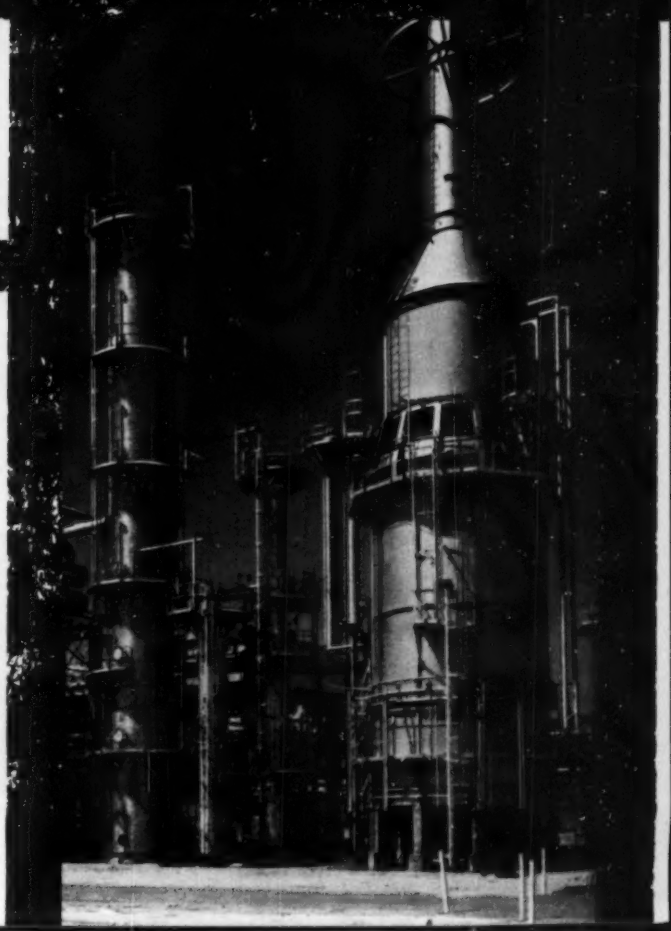

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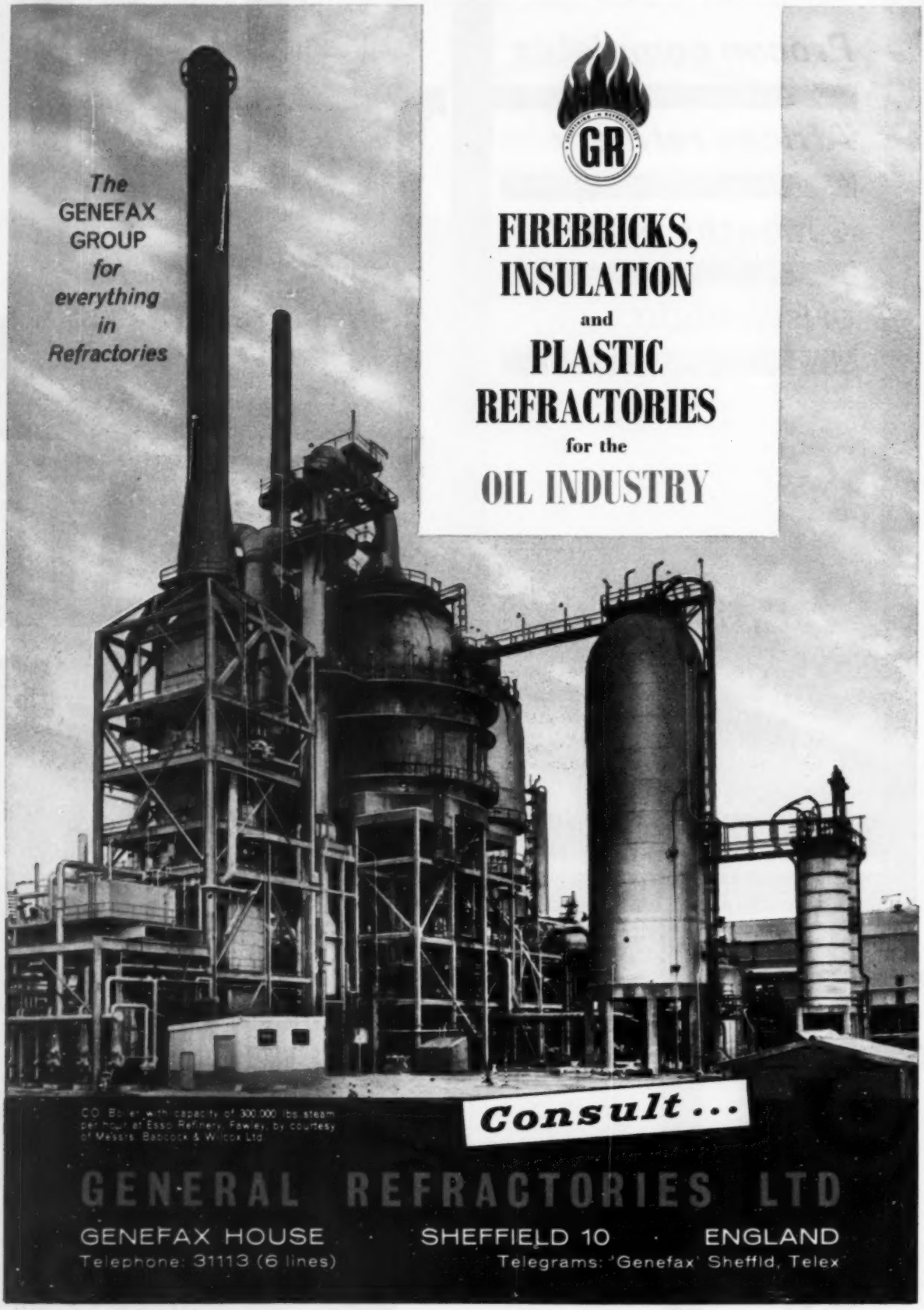
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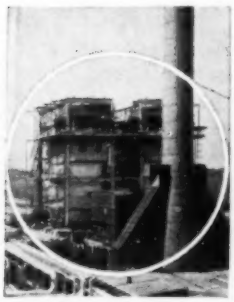

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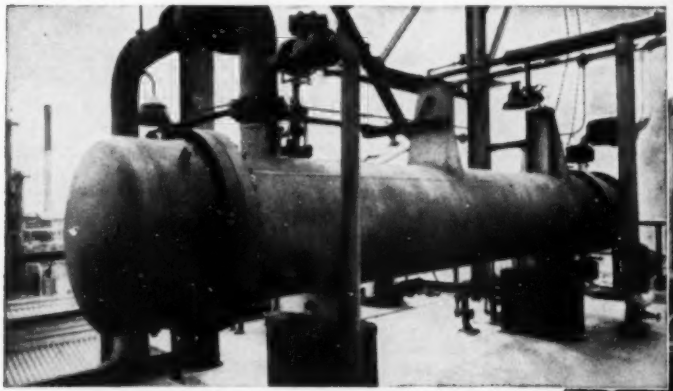
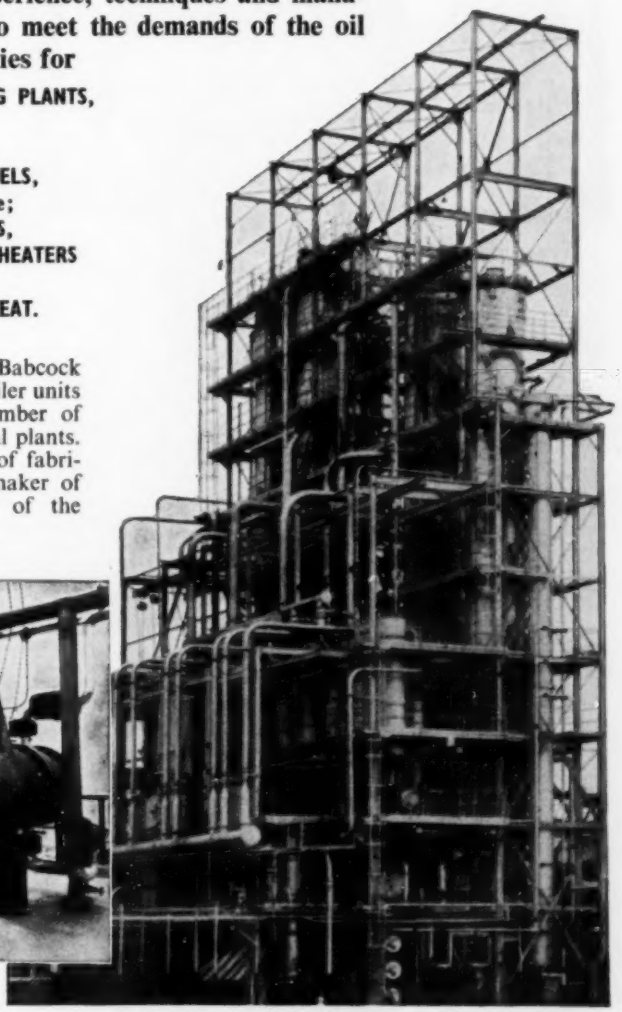


Heat-exchanger built by Babcock, in service at an oil refinery.



Distillation unit at an oil refinery, comprising Babcock fusion-welded columns.

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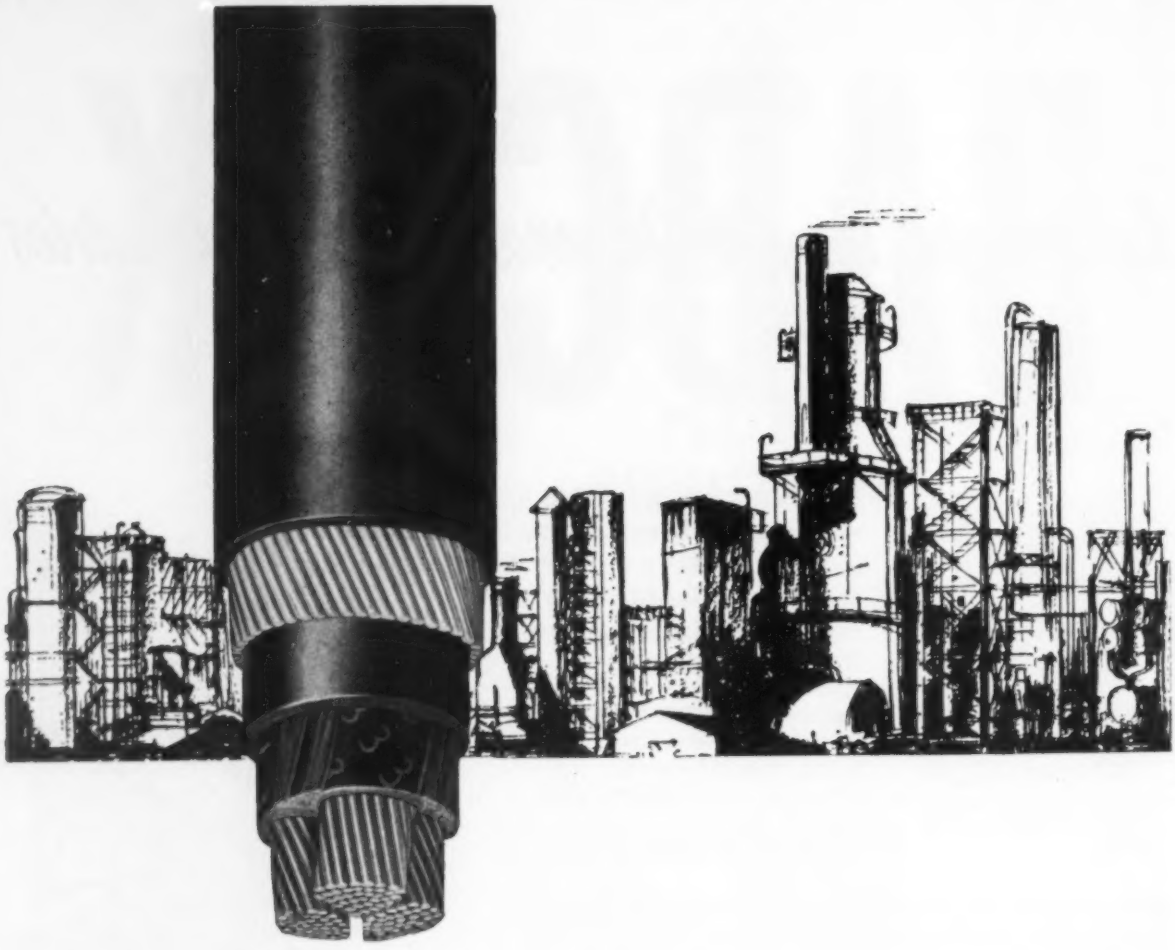

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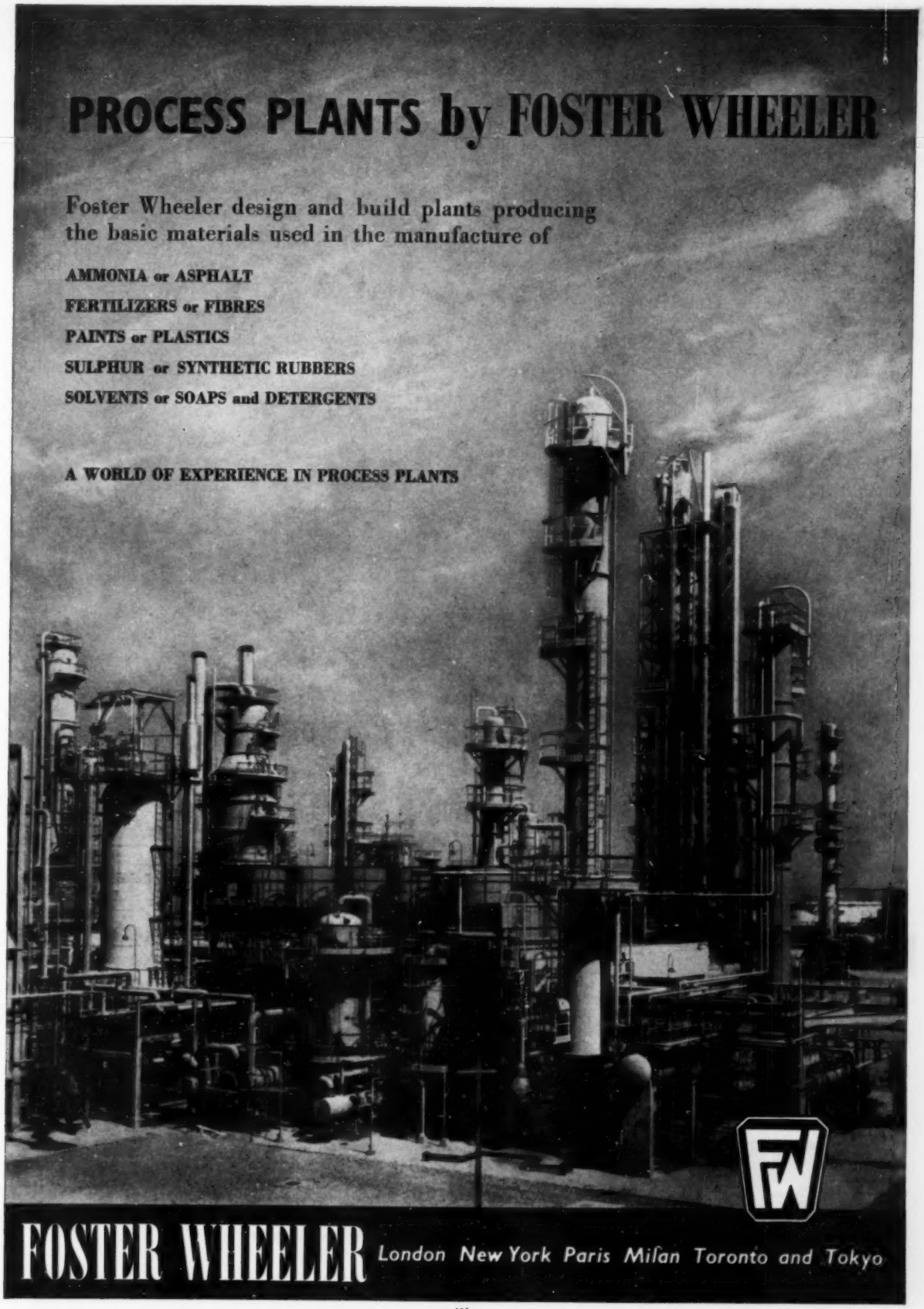
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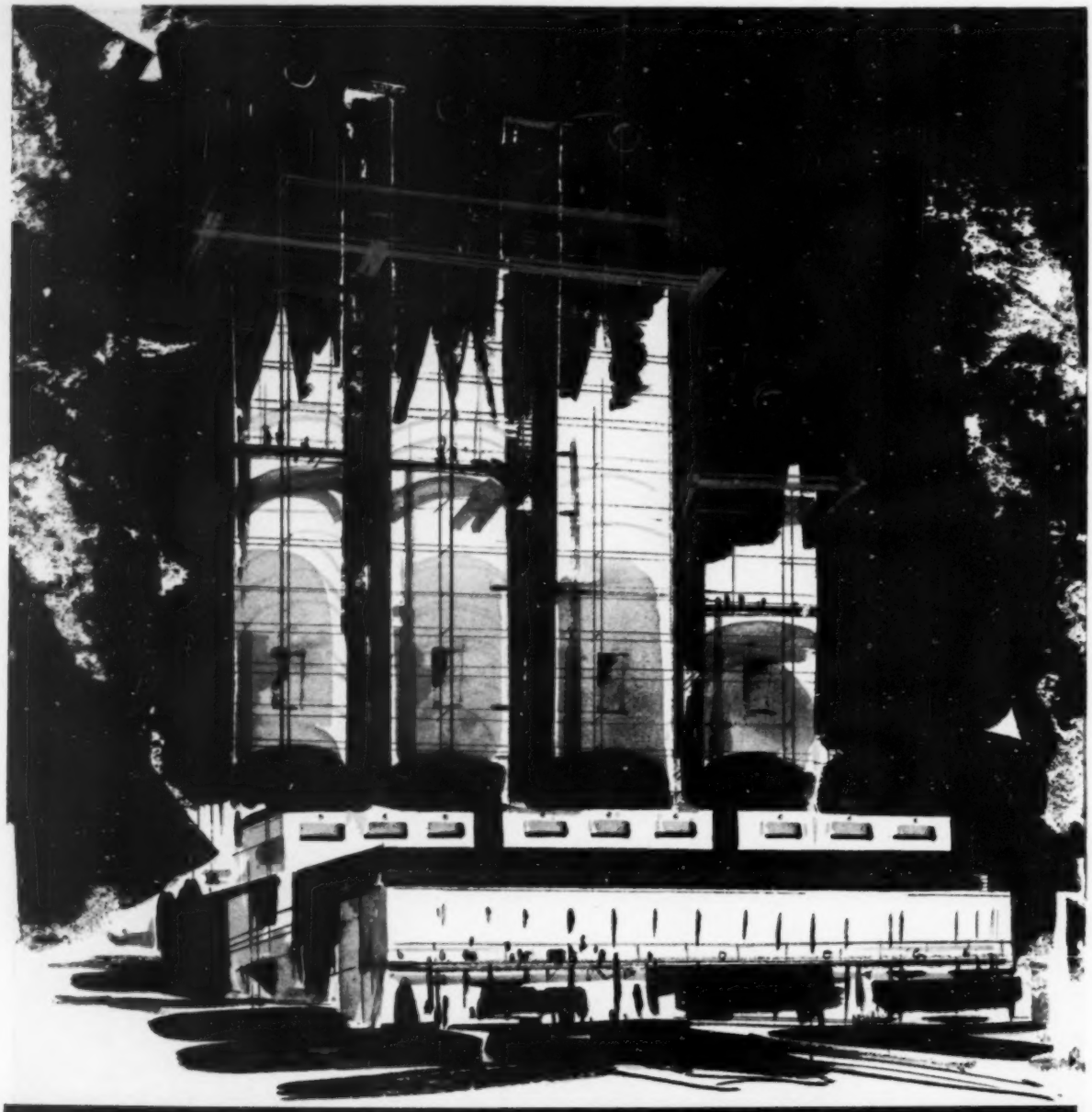

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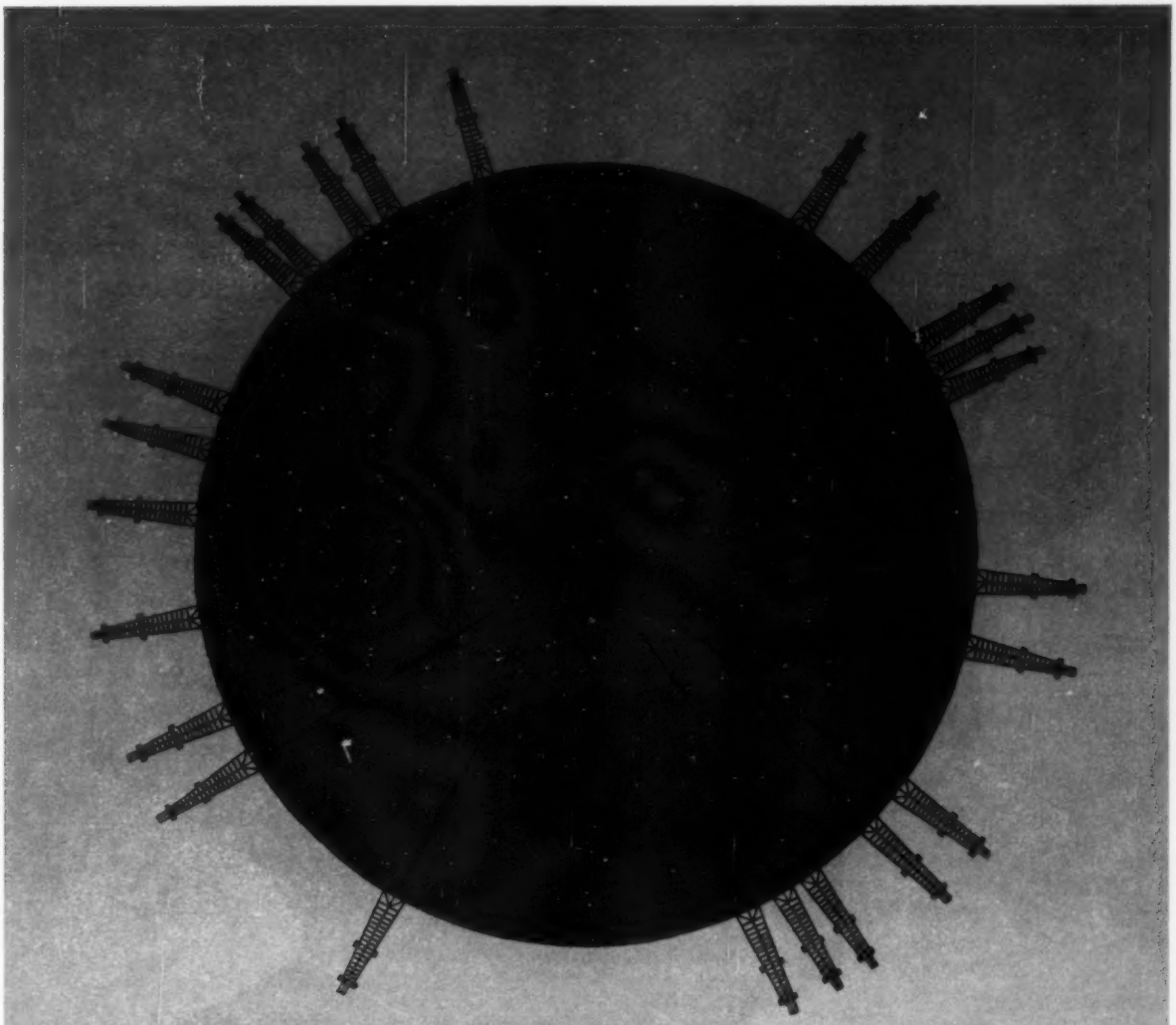

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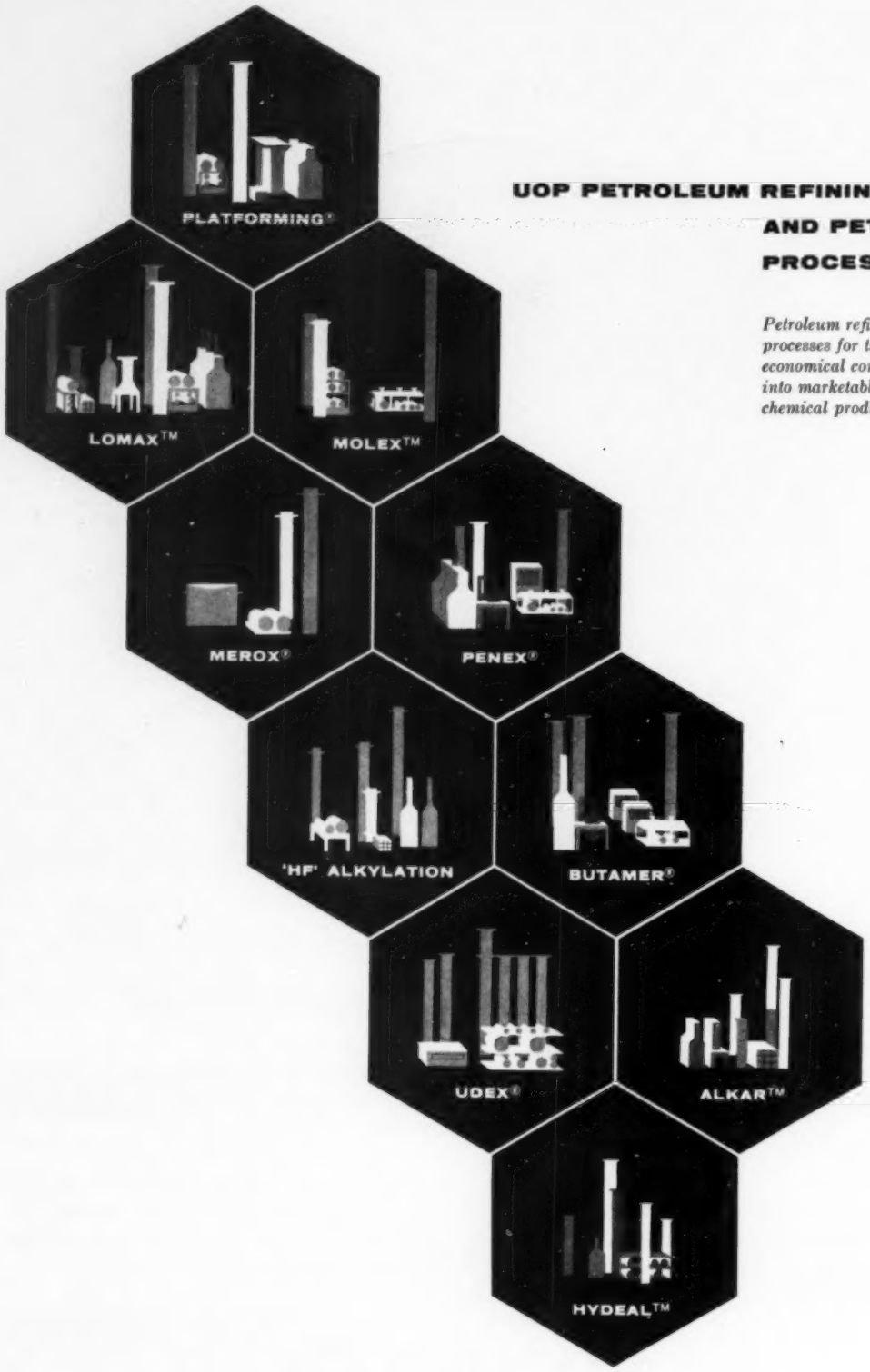

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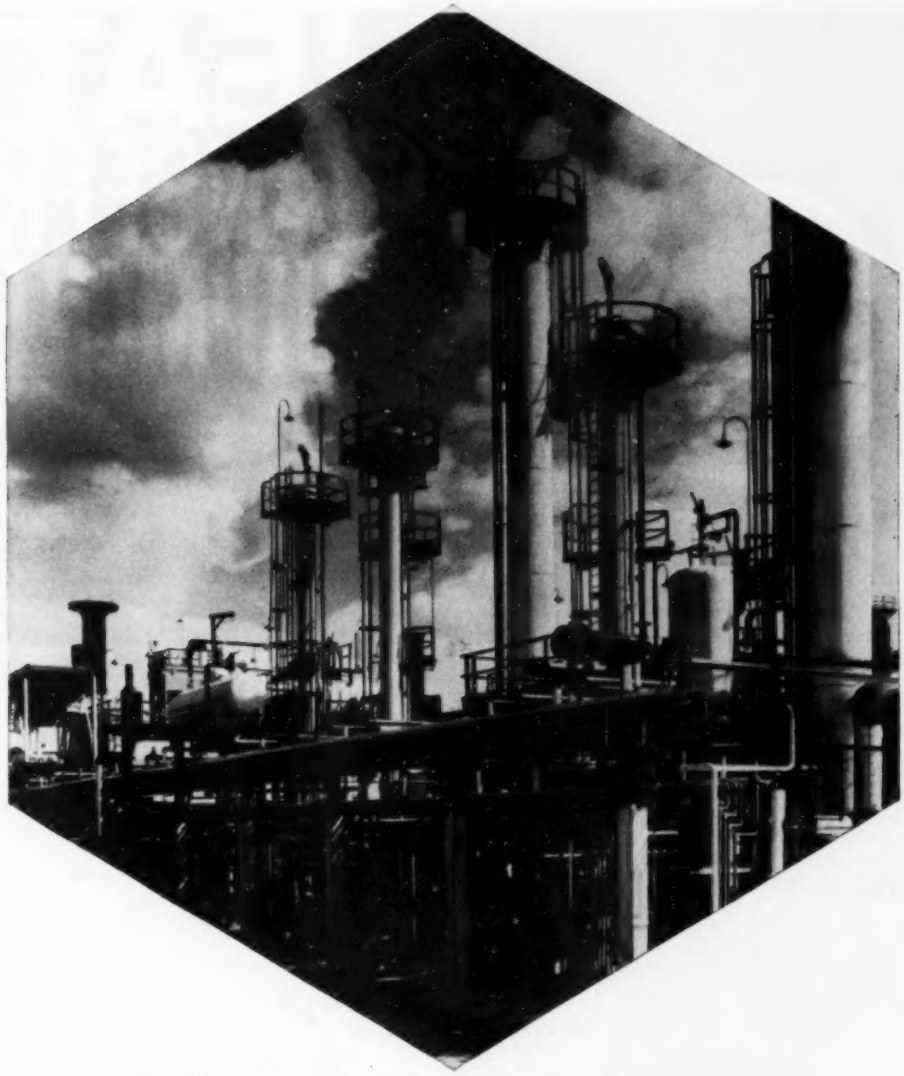

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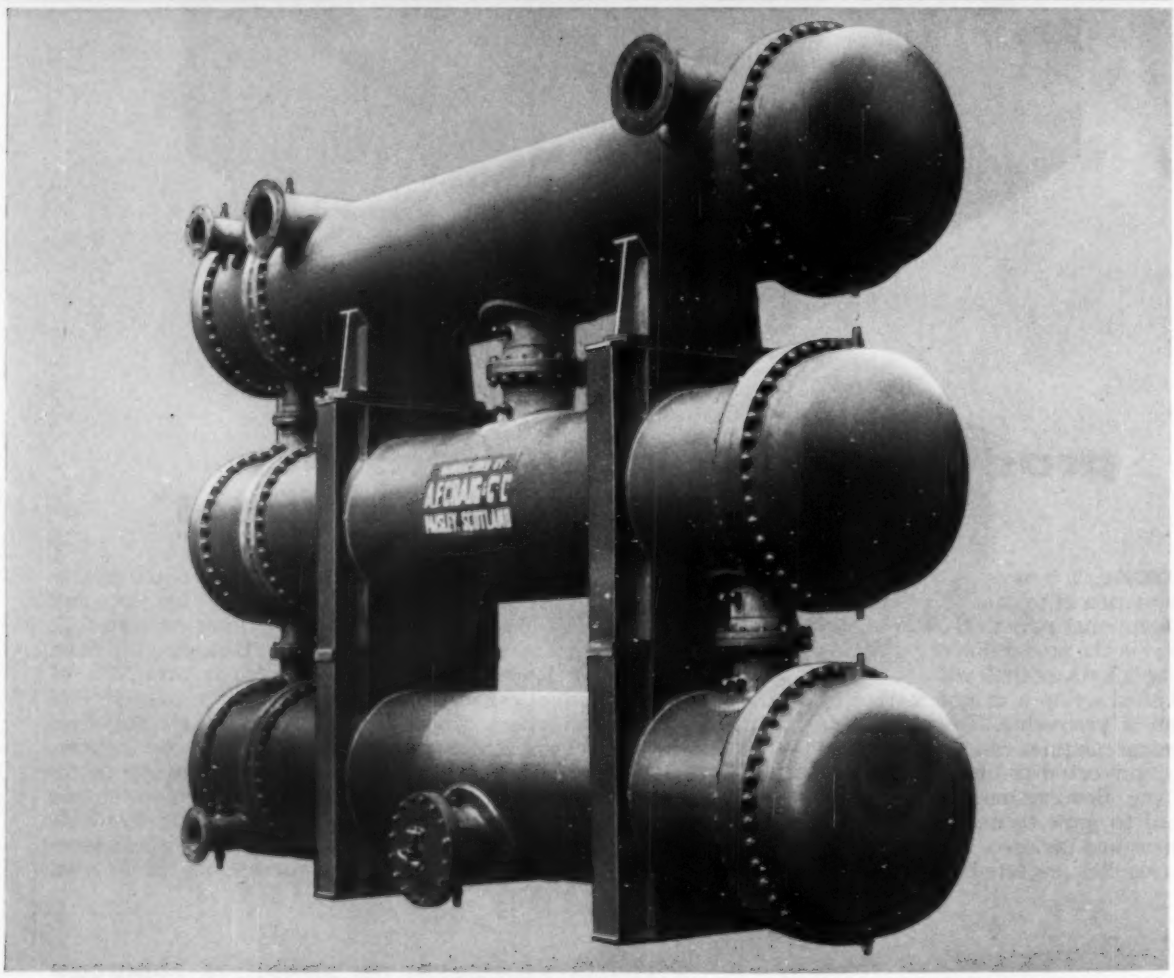

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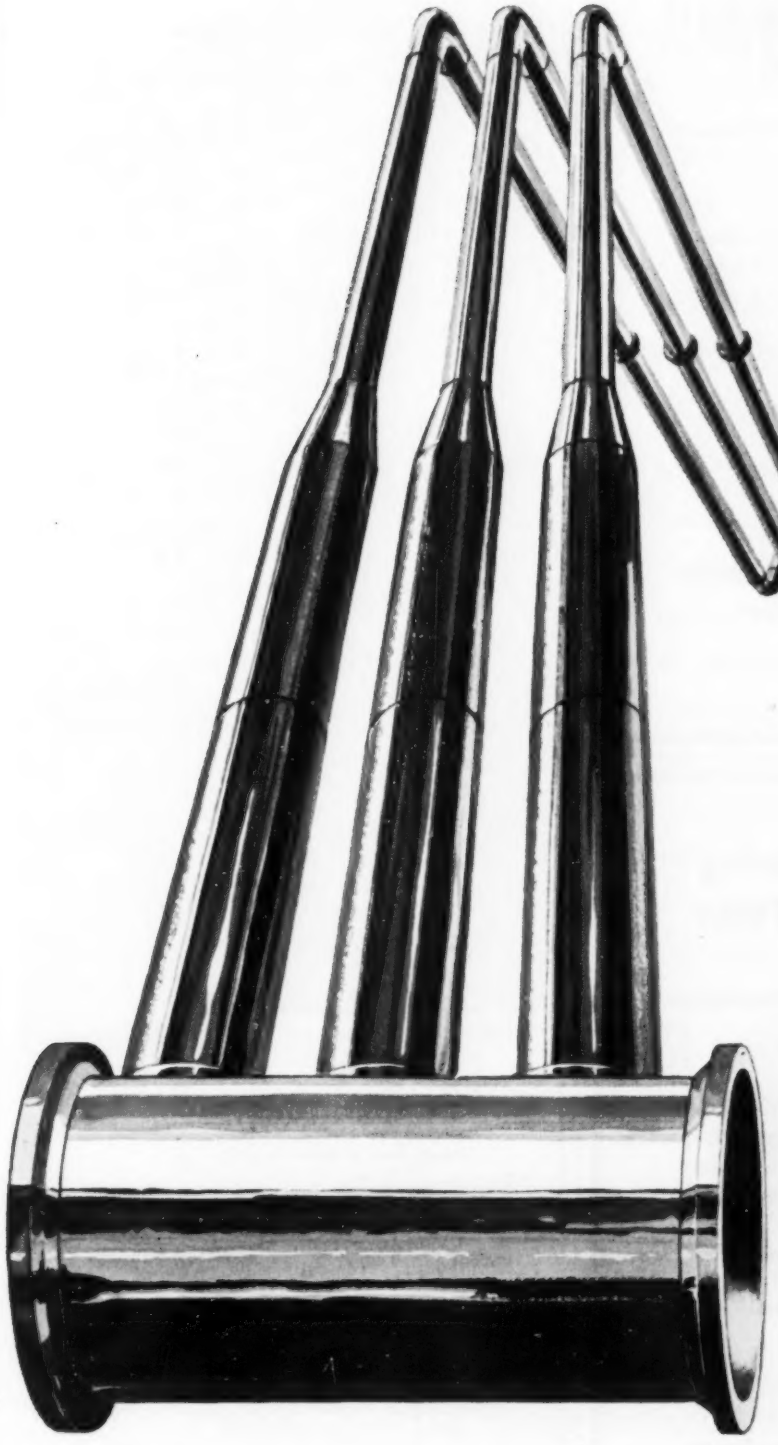

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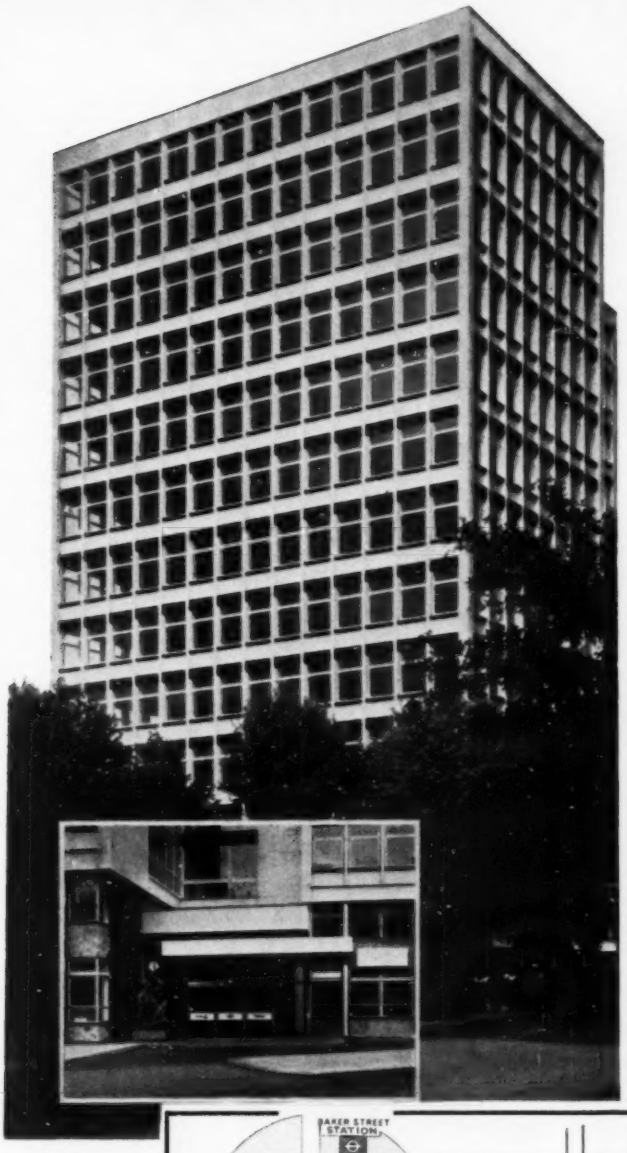

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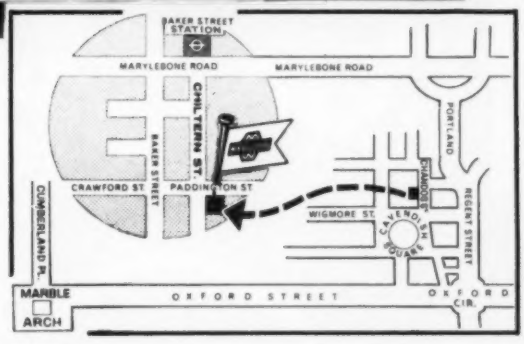

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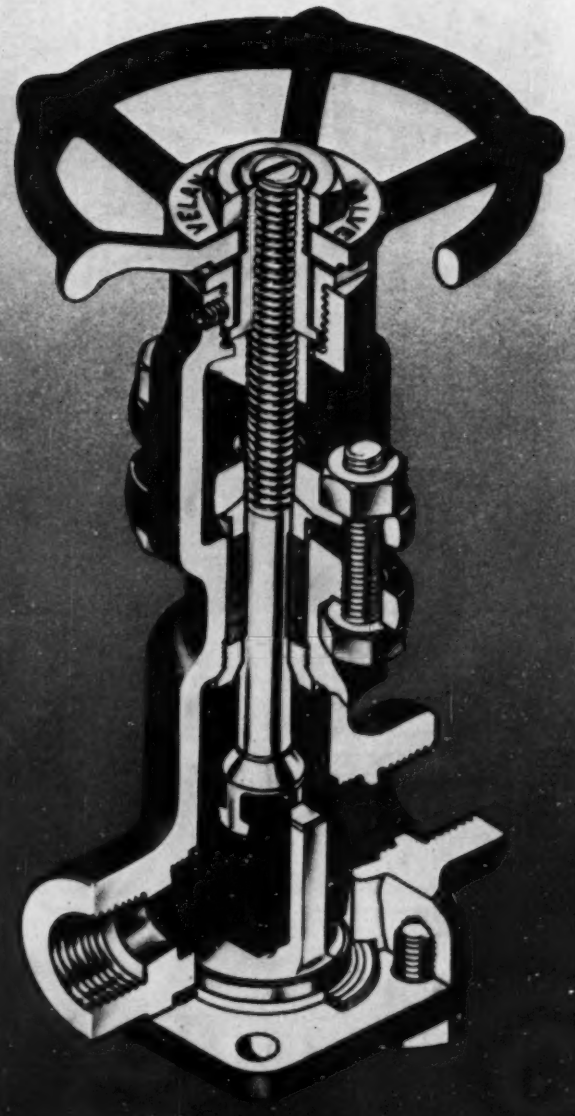

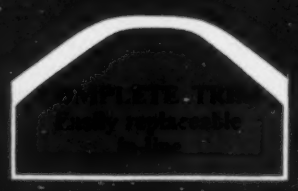

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